FUEL 1

New theory for basic water structure and potential fuel and energy applications

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A thermotropic liquid crystal consisting of a chain of 6 water molecules—a mixture of both the para nuclear spin isotopomer (para-water) and the ortho nuclear spin isotopomer (ortho-water)—is proposed as the "basic building block for water structure" (BBBWS). This structure, which is based on an a theoretical temperature-domain nuclear spin-flip spectrum for water, is the theoretical precursor to all other polymorphs of water (e.g., gas hydrate cages, hexagonal ice, snow flakes, and open and cyclical clusters containing 2 to 5 H2O molecules each). The nuclear spin-flip spectrum was derived from an equation relating the excess Gibbs free energy for the conversion of a mole of para-water to a mole of ortho-water to apparatus dehydration isotherm data obtained with a dew point hygrometer. The nuclear spin-flip transitions of the BBBWS are coupled to phonons, and low-frequency (terahertz) librations are coupled to the nuclear spin-flip transitions. This presentation will focus on three main subjects—(1) non-covalent, structure-determining, inter- and intra-molecular bonding in the BBBWS, (2) the theoretical nuclear spin-flip spectrum for water, including validation data, and (3) potential fuel and energy applications of the basic water structure theory. The potential applications to be discussed include "Kanzius effect combustion," which involves the use of RF radiation catalysis in the presence of an electrolyte such as NaCl to dissociate H2O molecules into an intimate mixture of H2 and O2 molecules which can be ignited and burned with a steady flame; the use of water to influence the capture of CO2 in power generation plants; and the prediction of the temperature dependence of the physical properties of gas hydrates (e.g., methane hydrates and CO2 hydrates).

FUEL 2

C-Cycle: Carbon dioxide capture, activation and product release

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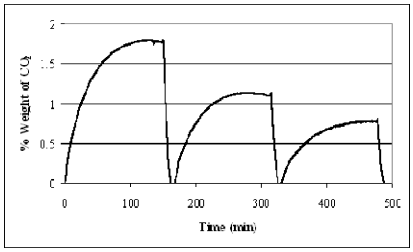
Energy from waste plants generate heat and electrical energy from domestic waste, thereby reducing reliance on landfill and fossil fuels. However, they still

produce CO_2 which adds to greenhouse emissions.



We report the results from our preliminary studies on carbon capture, using functionalized liquids as the host matrix; CO_2 activation through the use of novel catalysts; and release of the products from the matrix using pressure and temperature swing techniques. In particular, we demonstrate a practical method for the determination of vapor pressures on a micro scale using ionic liquids as the host.

Capture studies will show how the physical and chemical nature of the host matrix can affect the selectivity of CO_2 uptake and re-use over repeated capture-release cycles. We will also show how catalysts can be incorporated into the host, which activate the CO_2 towards reaction with additional species to yield commercially important organic feed stocks and fuels.

FUEL 3

Enhancement of surfactant on the dibenzothiophene biodesulfurization

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Biodesulfurization (BDS) with dibenzothiophene (DBT) or DBTs as the sulfur model compounds has been studied recently. It was indicated that the overall biotransformation rate depends not only on biokinetic factors, but also on physicochemical constrains that control the bioavailability, when an oil-bacteria-water emulsion is formed. Surfactants, as amphiphilic compounds, have desirable properties including solubility enhancement, surface tension reduction. Thus, surfactants such as soya lecithin (SL), Tween 80 and β-cyclodextrin (β-CD) were used in biodesulfurization by Mycobacterium sp. ZD-19 to enhance the mass transfer of DBT in this study. Additionally, the effect of surfactants on the cell growth was also investigated. The results indicate that these three kinds of surfactants would not inhibit the cell growth. Among SL, Tween 80 and β-CD, the 2-hydroxybiphenyl (2-HBP) formation with SL present was 58% more than contrast control (without addition of surfactant).

FUEL 4

A novel used lubricating oils refining technology using cold-stage separation (CSS) system

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A Cold-Stage Separation System (patent pending) was invented and developed to simultaneously separate impurities (toxic materials) and recondition valuable compounds from used automobile lubricant oil at a comparable low cost, as well as without deriving of undesirable by-products. A polar and non-polar duo-solvents combination was used for mixing and followed by a separation stage to remove impurities. The additives and hydrocarbon compounds then would be separated from the processed oil by the difference in boiling points. Solvents could be recycled from condenser for reuse.

The advantages of this system are eco-friendly (reusable solvents and hazardous waste reduction), cost-effective (low temperature and pressure), time saving (short process time) and energy conservation (recycle the non-renewable energy source) compared to other current recycling and reprocessing options for used lube oil. A treatment method based on a chemical-aided ultrasonic irradiation reaction is also proposed as the pretreatment step to remove toxin for better overall performances.

FUEL 5

Application of computational chemistry to combustion processes: Generation of reliable thermokinetic data for the aromatics oxidation mechanisms

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Since a few years our lab carried out studies concerning the development of thermokinetic sophisticated models of oxidation and auto-ignition in the low and intermediate temperature range (600-900 K) at high pressures (5-20 bar) for standard car gasoline components. These models are developed and validated using experimental data obtained from the lab's Rapid Compression Machine

(RCM). The purpose of these models is to predict the formation of unburnt pollutants exhausts.

Thus, the aim of this work is to determine thermokinetic data for molecules and reactions which are considered to be critical using computational chemistry. The studied molecules are o-xylene, toluene, cyclohexane, cyclohexene and hexene isomers. The oxidation schemes for these hydrocarbons are determined from the oxidation reaction products with the RCM: the species and the reactions for which we need data were identified. We present here the results obtained in the case of the toluene and o-xylene oxidation.

FUEL 6

Exploring the chemical reactivity of asphaltenes

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Most of the hydrocarbon derivatives from petroleum are used to produce energy by combustion, but very few percent are converted to industrially useful compounds by controlled reactions with oxygen or chlorine. The hydrocarbons have high C/H ratio and are inert to attack by most of the chemical reagents and reacts with oxygen and halogens only under the special conditions of radical initiated reactions. One of the major constituents of the heavy residual oils and asphalts is the asphaltenes. Asphaltenes are composed of condensed aromatic structures units bearing alicyclic sites substituted and connected to aliphatic chains with or without heteroatoms. The objective of this study was to investigate the reacting behavior of asphaltenes to understand the structural, chemical and molecular nature of asphaltenes. Relatively little is known about the effect of chlorination on asphaltene chemistry and structure. In an effort to increase this understanding, the reaction of asphaltenes with sulfuryl chloride (SO2Cl2) alone and in presence of an initiator, 2.2'-azobis-(-methylpropionitrile), commonly named as AIBN (azoisobutylnitrile), was carried out. Asphaltenes contain predominantly C and H atoms in the form of aromatic and aliphatic structures. Both can be reactive and that the aromatic structures may affect the reaction pathway. All reactions began with the formation of free radical from SO2Cl2 followed by the abstraction of H atom which provided reactive radical intermediates. The IR spectra clearly show the addition of Cl groups in aliphatic as well as in aromatic structure of asphaltenes. The compositional data generated by this work will enhance the understanding of asphaltene structure.

FUEL 7

Nanocomposite oxygen carriers for chemical looping combustion of sulfur-contaminated coal gas

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Chemical looping combustion (CLC) is an emerging technology for clean energy-production. In CLC, an oxygen carrier is periodically oxidized with air and then reduced in contact with a fuel. CLC is thus a flame-less oxy-fuel combustion without an air separation unit, producing sequestration-ready CO2-streams without significant energy penalty. However, a major hurdle towards technical implementation of CLC is the development of robust oxygen carrier materials.

We present a detailed study on Ni-, Cu- and Fe-based nanocomposites, with particular emphasis on their performance in combustion of sulfur-contaminated coal gas. In sulfur-free streams the carriers show stable and fast reduction and re-oxidation kinetics. Sulfur contamination results not only in sulfidation of the metal carrier component, but also in partial sulfidation of the support matrix, marginally altering the redox kinetics without, however, affecting carrier stability. Interestingly, the support sulfidation leads to a significant increase in the oxygen carrying capacity of the carriers.

FUEL 8

Rapid analysis of bound glycerides in biodiesel using fluorescence

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Biodiesel can be significantly contaminated with glycerol, mono-, di- and triglycerides due to incomplete transesterification and insufficient purification. The presence of these minor components can lead to serious engine problems and hazardous emissions. Limits for the permissible levels of glycerol, mono-, di- and triglycerides have therefore been outlined by American Testing and Standard Materials (ATSM) D6584. This method employs Gas Chromatography (GC) however, it has been considered complicated, expensive, as well as erroneous. The purpose of this research was to investigate a quantitative method that could be accurate, reliable, easy and cost effective.

Biodiesel samples analyzed by GC for free and bound glycerol are hydrolyzed to completion and tested for glycerol content using UV/Vis analysis. Values are used to indirectly compare TLC bound glyceride analysis to GC bound glyceride

analysis. Reliability of results, sample preparation, short analysis time and simple instrumentation make the methods ideal for biodiesel quality control.

FUEL 9

Systematic exploration of hydrogen atom transfers in alkyl, alkenyl, and functionalized radicals, as predicted by composite ab initio methods

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Kinetic modeling programs will play increasingly important predictive roles in fuel chemistry as the energetic landscape shifts over the next few decades. These programs largely depend on automatic mechanism generation approaches, which themselves rely on Evans-Polyani relationships to extrapolate kinetic behavior from thermodynamic properties, efficiently generating kinetic data for a large number of elementary reaction steps. Isomerizations (H-atom transfers) dictate much of low-temperature combustion; generated mechanisms must accurately model this temperature range, which has implications for alternative fuels and engine design. High-level composite ab initio methods (G3MP2B3) were used to model isomerizations in many reactive species, including alkyl, alkenyl, cycloalkyl, and oxoallyic (derived from aldehydes and ketones) radicals. While enthalpies of activation scaled with enthalpies of reaction in alkyl radicals, the correlation was not seen for alkenyl and oxoallylic radicals. The implications of non-Evans-Polyani behavior for the increasingly functionalized radicals derived from alternative fuels will be discussed.

FUEL 10

Waxphaltene Determinator for rapid separation of waxes and asphaltenes

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A new separation called the Waxphaltene Determinator is a solubility-based method that allows the detection of waxes and asphaltenes from mg quantities of sample in minutes. Waxes and asphaltenes are initially precipitated together on a ground polytetrafluoroethylene (PTFE)-packed column using a methyl ethyl ketone (MEK) mobile phase at -20 ºC. Following elution of the MEK soluble

material, branched and n-paraffin wax components with carbon numbers less than C20 are re-dissolved in heptane at -20 °C and they are eluted as a single peak. The column is then rapidly heated to 60 °C, and n-paraffins with carbon number greater then C20 and slightly branched paraffins are melted, dissolved and selectively eluted with n-heptane. Asphaltenes and very polar asphaltenes are subsequently eluted at ~30 °C using toluene and methylene chloride, respectively. Results with the new separation method were compared with differential scanning calorimetry results for wax determination, and the data correlated well. Gravimetric asphaltene precipitation data were compared with asphaltene peak area percentages from the new separation and a near linear correlation was observed.

FUEL 11

Using mass spectrometry to improve on the SARA analysis for a series of Canadian heavy oils

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SARA fractionation is an operational definition that can vary greatly in results depending on procedure. This study looks at three alternative methods to cross correlate SARA results and to further assess viscosity relationships. Cross Polarization Magic Angle Spinning ^{13}C Nuclear Magnetic Resonance (CP/MAS ^{13}C NMR) is used to assess aromaticity and the average aromatic clustering number, in hopes that the percent aromatics from the NMR experiments correlate to the SARA and that the average carbon clustering number relates to the viscosity. Gas-Chromatography Mass Spectrometry (GCMS) and Molecular Beam Mass Spectrometry (MBMS) was carried out on the six Canadian samples. A principal component analysis fitted with a partial least square regression line was done for the respective inputs to predict 20°C 10 Hz viscosity. Both methods predicted viscosity well with R-squared values around 0.9. The faster MBMS procedure is advantageous for correlating chemistry to viscosity and delivers adequate results describing the SARA fractions.

FUEL 12

Analysis of Maya crude oil

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Maya crude oil was separated into maltenes (heptane solubles) and asphaltenes (toluene solubles) and the asphaltene fraction was further separated into NMP-soluble and –insoluble fractions. These fractions were examined by SEC in NMP/chloroform eluent and by UV-fluorescence spectroscopy. LD-MS was used to estimate ion mass ranges after fractionation using TLC before exposure to the laser, to separate small and large ions. This allows the application of variable laser power to the small and large molecules separately; this method avoids exposure of small molecules to high laser power, since ionized cluster ions may form from small molecules and mask the large ions, in the absence of separation. The LD-MS results indicated that the most intense peak of the maltene fraction was below m/z 1000, but the peak masses for the asphaltene fractions increased up to m/z 2000, with high mass limits of around m/z 10,000, in reasonable agreement with SEC results.

FUEL 13

Nonpolar speciation of Athabasca bitumen by atmospheric pressure photoionization FT-ICR mass spectrometry

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The high resolution and mass accuracy of FT-ICR mass spectrometry allows the detailed characterization of compositionally complex petroleum samples at the level of elemental formula assignment. Examination of the heteroatom class, type (DBE), and carbon number allows for core structural determination. Here, we continue previous work to characterize middle distillate of Athabasca bitumen and have shown the global continuum. Petroporphyrins are detected directly for the first time, without prior extraction.

FUEL 14

Syncrude characterization

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An atmospheric residue from Athabasca bitumen sweet blend has been characterized using size exclusion chromatography, UV-fluorescence spectroscopy and mass spectrometry (GC-MS, heated probe-MS and laser desorption MS) to indicate the extent of the mass range of the material. The Athabasca bitumen is a more difficult sample than the Maya crude and should provide a more stringent test of the methods applied to the Maya. Fractionation of the sample was by solvent solubility into heptane solubles (maltenes) and toluene solubles (asphaltenes). The maltenes were separated into acetone-soluble and –insoluble fractions; the asphaltenes were separated into NMP-soluble and –insoluble fractions. TLC was used to separate these fractions before LD-MS. LD-MS and SEC gave mass range estimates increasing from maltene acetone-solubles through NMP-insolubles of asphaltenes up to at least m/z 10,000. The fractions containing the largest molecules had little or no fluorescence; fractionation proved essential to detect the largest molecules.

FUEL 15

Development of a drop-in unifuel/single battlefield fuel of high thermal stability

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The future of military transportation fuels has been an area of increasing interest. One of the proposed solutions is a fuel that can be used in both diesel and gas turbine engines as a single battlefield fuel or unifuel. The fuel needs to satisfy all of the current JP-8 specifications with two additional design constraints of higher thermal stability and an increased cetane number. Previous work has established a fuel with considerable thermal stability (JP-900 X1390). Using this fuel as a base compound, various solutions are considered and evaluated using an Ignition Quality Tester (IQT™) instrument. The focus of the study is two fold; the addition of trace quantities of cetane improvers such as Ethyl Hexyl Nitrate (EHN) and secondly increasing the concentration of fuels with desirable derived

cetane numbers (DCNs). The fuels used to dope JP-900 X1390 were B100, S-8, and Sasol Diesel. Additionally, NORPAR 13 and decalin are proposed as a first approximation unifuel surrogate. It was concluded that a mixture of decalin and long chain single branched iso-paraffins meet many of the design challenges presented in designing a unifuel. Finally, a general production scheme is proposed for the manufacture of this fuel.

FUEL 16

Structure-activity relationship in low temperature oxidation of cyclic hydrocarbons

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Low temperature oxidation (LTO) of four cyclic hydrocarbons is studied in a motored engine with controlled extent of oxidation. Conformational analysis is applied to the LTO chemistry to obtain a qualitative structure-activity relationship between the steric structures of these compounds and their LTO reactivity. The observed LTO reactivity is explained by the molecular steric structure and resultant hydrogen accessibility to the key chain branching step, (1,5) H-shift of fuel peroxy radical. LTO reactivity follows the same trend as the total number of hydrogens in a molecule that is available to (1,5) H-shift, and the degeneracy of (1,5) H-shift, i.e., the number of hydrogens available to (1,5) H-shift of a given peroxy group. MCH has the methyl group to preoccupy an equatorial position and forces the later formed axial peroxy group to stay at an axial position thus favors (1,5) H-abstraction.

FUEL 17

Proposed reactivity mechanism for trans- and cis-decalin and implications for the development of JP-900

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The future of transportation fuels requires development of alternative and unconventional resources in order to meet future demands. One of these alternatives is coal derivatives for the use in both turbine and diesel engines,

including fuels that can be used in both types of engines, i.e., a single battlefield fuel, or unifuel. The hydrogenation of refined chemical oil (RCO) and light chemical oil (LCO) produces decalin as the major product. Decalin has been shown to have desired thermal stability and much work has been done to characterize it as the major constituent of the coal-based jet fuel, JP-900. In the design of unifuels with decalin as the major constituent the autoignition character of the isomers of decalin was found to be the most important consideration. The derived cetane number (DCN) of cis-decalin was found to be 40 whereas the DCN of trans-decalin was 32.

FUEL 18

Affordable cellulosic ethanol by 2012: NREL's thermochemical platform R&D

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NREL's Thermochemical Platform strategic goal is to develop technologies for converting feedstocks into cost-competitive commodity liquid fuels, such as ethanol and advanced biofuels. The overall performance goal of the Thermochemical platform is to reduce the estimated mature technology processing cost for converting cellulosic feedstocks to ethanol via mixed alcohol synthesis to $1.33 per gallon by 2012, based on integrated pilot-scale data and a feedstock cost of $46/dry ton.

The challenges being addressed at NREL and its partner institutions fall into three broad categories:

• gasification of wood, biorefinery residue streams and low sugar content biomass

• syngas cleanup and conditioning

• development of fuel synthesis catalysts

This paper reviews the research and process development underway at NREL in each of these areas critical to meeting the 2012 goal of a fuel-grade ethanol production capability at a MSRP of $1.33 per gallon.

FUEL 19

Biomass characterization and organosolv pretreatment of Buddleja davidii

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Buddleja davidii, as a potential bioresource for biofuels, has several attractive agro-energy features. This research project constitutes the first detailed characterization of this novel biomass feedstock. Results from the biomass characterization of *B. davidii*, which includes the determination of lignin, hemicellulose, and cellulose contents, as well as, detailed elucidation of the chemical structures of both lignin and cellulose by NMR will be presented. Solid-state CP/MAS ^{13}C NMR has been used to study the structure of cellulose and structural characterization of lignin has been performed using quantitative ^{13}C NMR and ^{31}P NMR spectroscopy. Furthermore, *Buddleja davidii* was pretreated using the organosolv pretreatment technology and optimum pretreatment condition has been found. The mass balance at the optimum condition and the glucose recovery by enzymatic hydrolysis were determined. This talk summarizes the bioethanol production capabilities of *B. davidii* guided by its fundamental chemical biomass constituents.

FUEL 20

Chemical kinetic mechanism additivity

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The Utah Surrogate Mechanisms was used to study the combustion emission of a California gasoline fuel. Those published results are further examined in this study for chemical reaction mechanism additivity between different chemical classes. The 23-component surrogate used in the original study is divided into subsets, and these subsets of chemicals are modeled using the same mechanism under the same premixed flame experimental conditions as in the original gasoline study. The weighted sum of each species concentration is calculated according to the mole percentage distribution of each subset in the gasoline fuel. Different subset partitions are investigated. The simplest partition includes three subsets of olefins, aromatics and benzene/toluene/cyclohexane/MTBE. Each subset includes paraffinic fuel components to provide a similar radical pool that was obtained with a full surrogate. Two other partitions of 7 and 13 subsets are also studied. The weighted sums of each species using different partitions match very well the

predicted concentration of that species if a full surrogate was used. Therefore, chemical mechanism additivity is found to be applicable between different chemical classes.

FUEL 21

Development of detailed kinetic models for Fischer-Tropsch fuels

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Fischer-Tropsch (FT) fuels, which can be synthesized from a syngas stream generated by the gasification of biomass, have both the chemical and physical properties that are somewhat different from the petroleum-based hydrocarbons they might replace. For example, FT fuels contain very little, if any, aromatics and have high concentrations of iso-alkanes with one or two methyl branches to meet the pour-point specifications. Since the different composition might alter the performance of diesel engines and gas turbines, it is important to develop a mechanistic understanding of the combustion chemistry of these iso-alkanes. Models are already available for smaller branched alkanes such as isooctane, but additional efforts are required to properly capture the kinetics of the larger branched alkanes. The current study presents results of two aspects of this effort. In the first part, predictions of a new reaction mechanism containing additional reactions for 2,2,4,4,6,8,8-heptamethylnonane (HMN), a large iso-alkane, are discussed. The extension, which addressed both the high and low temperature chemistry of HMN, was done using the same reaction rate rules as for the iso-octane mechanism. The second part describes the development of new rate estimation rules for H abstraction and isomerization reactions based on high-level electronic structure calculations. Since the data set contains primary, secondary and tertiary C-H bonds, we can use the results directly to predict differences in the initial radical pool between n-alkanes and iso-alkanes. Future work will include rate rule calculations for b-scissions and alkyl + O2 reactions.

FUEL 22

Development of low temperature glycerol and ethylene glycol fuel cells capable of high energy density and complete oxidation

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Glycerol being the major byproduct of biodiesel production has very few large scale industrial uses that can compare with its production rate making it very inexpensive and abundant. In addition, its high energy density (6260 Whr/L) and low volatility make it a very attractive fuel for biofuel cells. Ethylene glycol shares some chemical and physical similarities to glycerol such as high energy density (5260 Whr/L) and low volatility and also has the potential of being an attractive fuel especially for biofuel cells that are exposed to extreme low temperature conditions. Traditional low temperature fuel cells have difficulty oxidizing fuels that contain more than one carbon allowing only simple and low energy density fuels such as hydrogen and methanol to be used. By harnessing the catalytic power of enzymes that can achieve direct electron transfer to a carbon electrode, a three enzyme cascade was developed to completely oxidize two complex fuels, glycerol and ethylene glycol, at the anode of a biofuel cell.

FUEL 23

Ethylene pyrolysis and the subsequent molecular weight growth reactions

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This study focuses on the pyrolysis and molecular weight growth reactions of ethylene under conditions relevant to reformer or SOFC operation (τ=1~5s, T=550~900ºC, P~0.8 atm). Ethylene was chosen since it is often the dominant olefin formed during hydrocarbon pyrolysis, and it is also known to lead to deposit formation. Ethylene conversions were observed to vary substantially over the range of conditions used. The major light products observed were H2, CH4, C2H2, C3H6, C4H6, and heavier species. The most abundant aromatic species observed were benzene and styrene. Although it appears that current kinetic model can properly account for the initial conversion of ethylene to butadiene, the prediction of other product distributions is not satisfactory. The overprediction of 1,3 butadiene is likely due to the fact that reactions of butadiene to form higher molecular weight products are too slow in the model.

FUEL 24

Low temperature partial oxidation of ethane and propane

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This work describes gas-phase flow-reactor experiments and modeling results for ethane and propane pyrolysis and partial oxidation. The experiments were carried out at an ambient pressure of 0.8 atm and a residence time of ~5s and 550-800oC. Addition of small amounts of oxygen decreased the onset of conversion by ~75K. This shift is well-predicted for ethane, while for propane the shift was over-predicted. Flux and sensitivity analyses point out that these results are very sensitive to the reaction of alkyl radicals with molecular oxygen. This improved prediction of ethane+O2 system is likely due to the use of the well-characterized ethyl+O2 sub-mechanism. On the other hand, the kinetic information of the analogous propyl+O2 system used in the mechanism was less certain. Therefore, the potential energy surface (PES) for propyl+O2 system was re-calculated using a higher level of electronic structure theory, namely CBS-QB3. New reaction pathways/species were found and included. In addition to the more accurate and complete PES, thermodynamic properties of species were improved. These improvements have led to substantial changes in the high-pressure rate constants. After accounting for the pressure effects, we anticipate improved predictions for propane.

FUEL 25

Ozonolysis of biodiesels in the presence of various low molecular weight alcohols

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Ozonolysis of methanol-transesterified vegetable oils was conducted in the presence of various low molecular weight alcohols at room temperature. GC/MS analysis of the ozone treated biodiesel showed that the double bonds in olive biodiesel molecules were being cleaved by ozone via direct electrophilic addition during reaction. Among all terminal carboxylic acid esters, the monocarboxylic acid esters and bicarboxylic acid esters with the carbon number from C6 to C9 were mostly generated from direct decomposition of α-alkoxyalkyl hydroperoxides during ozonolysis, but some of the esters were formed from reactions of oxidized aldehydes, another major products of ozone eletrophilic addition reaction, with low molecular weight alcohols. When other low molecular

weight alcohols such as ethanol instead of methanol were in the reaction phase, the reverse transesterification of methyl carboxylic acid esters by other alcohols was identified by GC/MS analysis. The fuel properties of biodiesels treated by ozone in other alcohols should be better than in methanol since the molecular structures of fuels are more complicate.

FUEL 26

Biodegradation effects on the molecular and isotopic compositions of petroleum columns: A case study from the Alberta tar sands

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Petroleum columns with progressively biodegraded bitumens from the Alberta tar sands were studied to assess the effects of biodegradation on the molecular and isotopic compositions of the oils. Molecular composition shows levels of biodegradation from 5 to 7 in the Peter and Moldowan scale, increasing from top to bottom of the oil column. No n-alkanes or isoprenoid alkanes were present in any of the bitumens. Polycyclic aromatic compounds and biomarkers such as steranes and hopanes were severely altered at the highest level of biodegradation. Aromatic steroids, tricyclic terpanes and pregnanes remain intact. Biodegradation does not cause observable variations in the carbon, nitrogen or sulphur isotopic compositions of bulk bitumen and no bulk carbon isotope changes were observed in fractions of different polarities. In general, the sulphur and nitrogen contents of the bitumens increase with increasing biodegradation levels. Isotope composition analyses of sulphur, nitrogen and hydrogen in fractions of different polarities are being conducted

FUEL 27

Calculations on model compounds for heavy petroleum constituents

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Although petroleum contains over a million different molecules, most of this diversity is found in its heavier fractions. They usually contain constituents capable of self organization making the separation and identification of individual molecules an almost hopeless task.

In order to circunvent these difficulties, petroleum and its derivatives may be separated in solubility classes and the heptane - insoluble constituents may be further fractionated.

FUEL 28

Catalytic cracking of residual oil with iron–based catalyst in a steam atmosphere

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Catalytic cracking of atmospheric-residual oil with zirconia-alumina-iron oxide catalyst at 450-500ºC in a steam atmosphere was examined to recover lighter fuels as much as possible. Heavy oil fractions were decomposed by attack of the active oxygen and hydrogen species generated from steam over the catalyst, and lighter fuels, such as gasoline, kerosene and gas oil, were generated without any coke at *W*/*F* (ratio of catalyst to feedstock) of 1.6-2.7 h. The amounts of lighter fuels increased with increase in temperature and *W*/*F* because the large amounts of active species generated from steam were reacted with heavy oil fractions. The largest amounts of lighter fuels (about 40 mol%-C) were obtained with *W*/*F* of 2.7 h at 475ºC, and *W*/*F* of 1.6-2.7 h at 500ºC.

FUEL 29

Compatibility and stability characteristics when blending different diluents and bitumen crudes

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The Canadian oil sands will become a key source of future crude supply. The bitumen must be diluted with a lighter hydrocarbon stream to meet the specifications required for shipping in pipelines. Compatibility and stability characteristics when blending diluents and crudes are important issues in the pipeline transportation. Four typical bitumen crudes and three diluents, i.e. natural gas condensate (NGC), oil sands derived liquid and n-alkanes, were chosen to investigate their compatibility and stability characteristics. For each crude and diluent, their physical and chemical properties were analyzed. Following oil compatibility model developed by Irwin Wiehe, the insolubility number and solubility blending number of different crudes, diluents and their blends were studied. As well, the asphaltene stability of crudes in different diluents was further investigated using an optical method (ASTM D-7061). The calculated separability number was used as a parameter to measure the stability. The results of compatibility indicate that oil sands derived liquids are better solvent for Athabasca bitumen than NGC. However for cracked Athabasca bitumen, even at low ratio, both oil sands derived liquids and NGC resulted in incompatibility. The asphaltene stability studies suggest that NGC is a better solvent for cracked Athabasca bitumen, and oil sands derived solvent is a better solvent for Athabasca bitumen.

FUEL 30

Desulfurization process of heavy fuel oil

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Intermediate fuel oil and residual fuel oil are heavy fraction usually having high viscosity as well as high sulfur contents (>1.5%). Since conventional hydrodesulfurization (HDS) process requires high temperature, pressure and high capital cost, common practice for combustion needs blending with low sulfur fuel oil and severe scrubbing. At present the sulfur limit allowed for residual fuel oil is from 1.5% to 4.5%.

Recently we have developed a new oxidative desulfurization method by using solid metal superoxide with an appropriate pair of ionic liquids. Intermediate fuel oil, as well as residual oils (Bunker Oil No. 6), the average desulfurization efficiency is 65% within 3 hours at 70˚C, in ambient pressure with stirring. Through the work we found that asphaltene in the heavy oil inhibited the oxidation process. We have developed some unique methods to combat this fact. The overall approach increases the desulfurization efficiency.

FUEL 31

Exhaust emission and combustion behavior of Fischer-Tropsch fuel in a compression ignition engine

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In this study, Fischer-Tropsch (FT) fuel with a high cetane number (>78) was investigated along with the ultra low sulfur diesel fuel (BP15). Physical, chemical, and compositional properties of FT fuel and BP15 were investigated and tabulated. With FT and BP15 fuelling, a common rail direct injection diesel engine was operated at 2400 rpm with low (64 Nm) and high (110 Nm) load. The engine performance, gaseous and particulate matter emissions, combustion behaviors, and particle size distributions were compared and discussed. With fixed start of combustion, FT fuelling showed similar NOx emissions, but lower HC, CO and particulate matter emissions as BP15. FT fuelling also showed lower particle concentration and a smaller mean particle diameter.

FUEL 32

Regional and local scale GIS surface and groundwater models of the oil shale basins

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Regional and Local Scale GIS Surface and Groundwater

Models of the Oil shale Basins

Hydrologic and Geochemical Baseline data was transferred between the BLM and USGS in 1985 by me for Hydrogeologic Modeling studies being conducted on the Oil Shale basins in Colorado, Wyoming, and Utah. This data which was lost in the last 20+ years since the Oil Shale boom in the 1980's, is presented here in a GIS presentation in coordination with current GIS models of the basins as they exist today.

The use of this data is discussed with current events.

This is a long presentation. Therefore some of the slides will be discussed in greater detail according to the amount of Oil Shale development activity present or amount of analyzed data in that area.

FUEL 33

Synthesis and characterization of heteropolyacid immobilized membranes

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Lacuanary heteropolyacids ([α H8SiW11O39].14H2O) (HSiW) have been immobilized in a perfluorosulfonic acid (PFSA) polymer with pendant side chain –O(CF2)4SO3H on silica a support using sol-gel method. To obtain strong covalent bonds between HSiW and silica, HSiW has been used as the acid to hydrolyze tetraethyl orthosilicate. Infrared spectroscopy revealed a strong interaction between the silica source and the HSiW. The surface morphology of the membrane, studied using the Scanning electron microscopy and Atomic force microscopy, showed that the uniformly dispersed inorganic HSiW particles immobilized in the membrane have size range of 50-100 nm. The X-ray diffraction data revealed that the heteropolyacids exhibited an amorphous character in the ionomer matrix evident from the broadening of the HPA peaks. Proton conductivity of the HSiW loaded as well as the control membrane has been obtained at 100, 80 and 30% relative humidity in the temperature range of 50-120 0C. The conductivity of the HSiW immobilized membranes increased with the increase in temperature and humidity and was observed to be higher than the control PFSA ionomer membrane. A significant increase in the proton conductivity, nearly 1.75 times that of the control membrane is obtained at 30% RH for the 5% and 10% loading membranes. A practical proton conductivity of 0.2 S/cm was observed at 120 0C and 80% relative humidity.

FUEL 34

Novel polyoxometalate containing membranes for PEM fuel cells

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Current proton exchange membrane (PEM) technologies are inadequate to address the projected needs for fuel cell performance above 80 ºC. In order to address the challenge of operating a fuel cell at elevated temperatures, different proton carriers are needed. In this work, several polyoxometalates (POM) were chosen to serve as the proton carriers in three different polymer hosts suitable to serve as PEM fuel cell membranes. These membranes were loaded with POM that possessed a suite of differing counterions. The effect of the nature of the counter cations associated with the POM had on the organization of the carriers within the host polymer matrix was determined using scanning electron microscopy. The results of these studies will be presented.

FUEL 35

Triazole bearing sol-gel membranes as water free proton exchange membranes for hydrogen fuel cells

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Water free, proton conducting, free-standing membranes have been synthesized by incorporating triazole containing tetracyclosiloxanes into a PEG-TEOS based sol-gel matrix. The absence of any unbound PEG or cyclic siloxane was confirmed by 1H-NMR and the chemical structure of the membranes was corroborated by FTIR spectroscopy. TGA analysis indicated that the membranes are stable up to 250 °C and DSC analysis showed complete suppression of PEG crystallization after incorporation of the triazole containing cyclosiloxanes. The crosslinked membranes showed proton conductivities higher or comparable to those observed for the liquid, polysiloxane analog, notwithstanding the lower charge carrier density of the sol-gel membranes and the pronounced improvement in mechanical strength compared to the linear polysiloxanes. These results suggest that incorporation of small proton conducting molecules into an

inert sol-gel matrix may reduce the coupling between mechanical strength and ion transport ability, providing a new pathway for mechanically robust, water free, proton conductive membranes.

FUEL 36

Theoretical predictions for novel membranes for high temperature H2 purification: Amorphous films and dense sulfides

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Metal membranes are in many regards an ideal means of purifying hydrogen from mixed gas streams. One important theme in experimental studies of metal membranes has been to reduce membrane thicknesses in order to increase hydrogen permeation rates. A second, equally important, theme has been the search for materials that yield high hydrogen permeabilities under practical operating conditions. Historically, most work of this kind has focused on crystalline metal alloys. In this presentation, we examine two novel classes of materials, amorphous metals and dense metal sulfide, to assess whether they have promise as membranes for hydrogen purification. For both materials, performing experimental studies would require large resources to be invested simply to fabricate pinhole free films, a necessary prerequisite for examining a material's performance as a membrane. To avoid this requirement, we have used quantitative first-principles calculations to make predictions about defect-free materials.

FUEL 37

Properties of palladium-ruthenium membranes produced by electroless codeposition

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Cold-worked membranes made of palladium and ruthenium have been shown in the literature to have several advantages over pure palladium in hydrogen separation applications, in particular enhanced tensile strength and resistance to hydrogen embrittlement at low temperatures. In order to minimize cost and maximize hydrogen permeability, however, the films must be made thinner than

is typically possible in cold-working. An EDTA-free electroless codeposition bath was developed that can apply films of 0-10 wt% Ru onto any appropriately activated surface, producing highly-selective composite membranes as thin as 1.4 microns. Films consist of two phases at room temperature, an HCP ruthenium-like phase and an FCC palladium-like phase. Deposited composition is slightly Pd-enhanced over the bath composition. Pure-gas permeation testing shows H2 permeabilities similar to those of pure Pd. Nanoindentation hardness testing showed that a 5 wt% Ru alloy was 80% harder than a pure Pd membrane fabricated by the same technique.

FUEL 38

Using first-principles calculations to screen ternary alloys as membranes for high temperature hydrogen purification

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Using metal alloys offers a useful means of developing dense metal membranes for purification of hydrogen at high temperatures. Systematic screening of multicomponent alloys experimentally, however, is a resource intensive activity. To accelerate experimental efforts to identify alloys with superior performance as membranes, we have used quantitative first-principles calculations to make predictions about both the bulk and surface properties of binary and ternary Pd-based alloys. In this presentation, we will discuss our recent efforts to examine the bulk properties of Pd-based ternary alloys and the surface chemistry of CO on PdAu alloys.

FUEL 39

Performance improvement for palladium alloy membranes for hydrogen production

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Composite membranes, consisting of a thin Pd-Au alloy film supported on a robust, commercially ready porous substrate, have been investigated as a means of improving resistance to hydride phase formation and increasing performance

in purification of hydrogen from water-gas-shift (WGS) reaction mixtures. The hydride phase of Pd and Pd alloys have different lattice constant than the metal, and this difference leads to cracking of the membrane. In pure Palladium the hydride phase is formed when Hydrogen is introduced at temperatures below 300°C. Using a Pd-Au alloy the temperature at which the hydride phase is formed is greatly suppressed to ~100°C depending on composition. Also, for use in hydrogen production from WGS reaction mixtures, alloying palladium with gold reduces the reduction in hydrogen flux caused by CO and H2S. Performance of the alloy membranes is discussed with respect to gold content in the membrane.

FUEL 40

Ab initio studies of palladium-niobium alloys for hydrogen separation

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Palladium-based membranes have been studied extensively for their application in H2 production due to their high permeability and catalytic activity to H2, their impermeability to other gases, and their stability at relatively high temperatures. However, a significant technical barrier impeding hydrogen separation membrane development is the susceptibility to Pd membrane deactivation via sulfur poisoning. Although desulfurization technologies can decrease the level of H2S present in an effluent stream down to the ppm range, these resulting trace concentrations still cannot be tolerated by Pd-based membrane materials. Alloying materials can allow one to tune a surface so that it exhibits the desired electronic properties necessary for a given catalytic process to take place. In this work alloys of PdNb are investigated to understand the mechanisms involved in surface site stabilities, reactivity, and subsurface hydrogen diffusion. Niobium is an optimal material to use because it has the highest hydrogen permeability of any other material and under specific conditions can be an order higher than pure Pd and has shown to be resistant to sulfur poisoning. Unfortunately, Nb is notorious for undergoing hydrogen embrittlement and can be a major structural issue that will also be examined through alloying. Density functional theory (DFT) is employed using the software package Vienna ab initio Simulation Package to calculated binding energies of hydrogen and sulfur in alloys of Pd and Nb. Surface and bulk properties of materials composed of transition metals can be understood through a complete density of states analysis and the reactivity can often be predicted using the “d-band center shift” model of Hammer and NØrskov. The local density of states (LDOS) of the s- p- and d-orbital states of the individual atoms is calculated to provide an understanding of the binding mechanisms associated with hydrogen and sulfur.

FUEL 41

Energy and hydrates: An overview inside the flowline and in nature

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This paper specified hydrate structures, as an introduction to the other papers of this symposium. In addition, two main applications of flow assurance and energy production are discussed in a preliminary way.

FUEL 42

Japan's national gas hydrate program

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The MH21 Research Consortium in Japan was organized to accomplish the 18-year National Methane Hydrate Exploitation Program for the exploration and exploitation of methane hydrate (MH) in the Eastern Nankai Trough of offshore Japan. In this program, the 2D and 3D seismic surveys as well as drilling of 32 exploration wells were conducted during 2001-2004.

The group for the resources assessment of this Consortium has been analyzing the data acquired through these surveys and drilling, and estimated the methane in place in MH resources in the Eastern Nankai Trough at about 40.3 tcf by Monte-Carlo simulation. In response to the above analyses, the group for the production method & modeling predicted MH dissociation/production performances through numerical simulation, followed by simple economic analyses, which exhibited the promise that some MH reservoirs in the Eastern Nankai Trough could be economically developed if the well spacing and MH dissociation/production methods were appropriately designed.

FUEL 43

India's national gas hydrate program

***VK. Sibal**, Director General of Hydrocarbons, India, Noida 201 301, India*

This keynote address will provide an overview of the state of the art of the Indian national gas hydrate program. The results of the recent successful expeditions will be highlighted during this presentation.

FUEL 44

China′s national hydrate program

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The People′s Republic of China is exploring alternative sources of energy to sustain them into the future. Gas hydrates, which are interpreted to exist in the Chinese offshore of the South and East China Seas, offer such a potential unexplored and unexploited energy source. A brief overview is given on the gas hydrate-related research activities carried out by Chinese researchers in the past two decades. The projects (863 Program, 973 Program, National Program) on fundamental studies and on exploration of natural gas hydrate resources in the South China Sea, which have been supported by Natural Science Foundation of China (NSFC), Ministry of Science & Technology (MOST), Chinese Academy of Sciences (CAS), etc, were introduced. There are nearly 40 groups engaged in gas hydrate research among China, most of which such as China University Petroleum (CUP), Guangzhou Center for Gas Hydrate Research (CASHYD), CAS, China Geological Survey were briefly introduced. Also, the future development and research have been mentioned.

FUEL 45

Overview of energy-related studies of gas hydrates in Canada

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Canada has been involved in assessing the energy potential of gas hydrates since the 1970's when the Geological Survey of Canada (GSC) assisted industry in appraising problems encountered during exploratory drilling in the Arctic. This work led to the first regional studies of permafrost gas hydrates in the 1980s and preliminary resource estimates in the 1990s. On Canada's Pacific coast GSC researchers first discovered the widespread characteristic gas hydrate bottom-simulating reflector in multichannel seismic surveys in 1985. Since then there has been extensive multi-disciplinary surveys/studies by GSC, Canadian universities, and international scientists on Canada's west and east coasts. Two ODP/IOPD

expeditions have been dedicated to sampling and measuring gas hydrates off Vancouver Island.

Over the past decade Canada has played a leading role internationally in hydrate production technology, improving geophysical detection techniques, and undertaking laboratory investigations of geologic controls. In 1998, the GSC, in partnership with the Japan National Oil Corporation, recovered the world's first Arctic gas hydrate-bearing core samples from the Mallik site, Mackenzie Delta. This program defined a highly concentrated, reservoir-scale occurrence of gas hydrates within a potentially producible porous sand matrix. In 2002, a five-nation international research consortium (Canada, Japan, USA, Germany, India) conducted large- and small-scale production experiments at Mallik to evaluate the efficiency of pressure reduction vs. heat stimulation for initiating in situ dissociation of gas. These experiments, along with state-of-the-art well logging and extensive post-field laboratory studies, provided critical scientific and technical data supporting the design and engineering of a subsequent Canada-Japan extended production testing program conducted during the winters of 2007/2008. In March 2008, 6 days of continuous methane production were achieved by depressurization of a concentrated gas hydrate interval. The Mallik test results have been widely acknowledged as “Proof of Concept” for the production of methane from hydrates by the depressurization method.

FUEL 46

Gas hydrate energy resource studies in the United States

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In 1982, scientists onboard the Research Vessel Glomar Challenger retrieved a meter-long sample of massive gas hydrate off the coast of Guatemala. This sample became the impetus for the first United States national research and development program dedicated to gas hydrates. By the mid 1990s, it was widely accepted that gas hydrates represented a vast storehouse of gas. Recognizing the importance of gas hydrate research and the need for coordinated effort, Congress and the President of the United States enacted Public Law 106-193, the Methane Hydrate Research and Development Act of 2000. Many of the current gas hydrate projects in the United States are focused on improved characterization of hydrates in the natural environment in order to develop the technology to allow production of gas from hydrates. A primary goal of the United States methane hydrate program is to investigate hydrate occurrence in the field.

FUEL 47

Applications of pair distribution function analysis to study energy-related materials

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The development of strategies enabling the economic implementation of alternative energy resources represents an important step toward our long term energy security. However, due to the often complex nature of unconventional fossil fuel resources or materials enabling new energy technologies, it is often challenging to structurally characterize these systems. Recently, the pair distribution function (PDF) method has emerged as a powerful tool to probe local structural information independent of long-range order. Our recent X-ray PDF studies of energy-related materials will be presented, including in-situ high pressure PDF studies of an oil shale - a highly complex organic-inorganic composite - for which it was possible to quantitatively evaluate the compressibility, even in the absence of a structural model.

FUEL 48

In situ NMR and pair distribution function studies of local structure in silicon anodes for lithium ion batteries

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Here, we demonstrate the use of various local structure probes, such as in-situ and ex-situ Solid State NMR and ex-situ X-ray PDF and analysis, to understand the structural changes that occur on lithiating bulk and nanoparticulate silicon anodes, when used in lithium ion batteries. Crystalline silicon undergoes a crystalline to amorphous phase transformation in the beginning of the first discharge when it is cycled versus Li metal. A long plateau at 0.09V vs. Li is seen, which is associated with the formation of a lithiated amorphous phase, (a)-LixSi. Larger particles then crystallize to form the metastable intermetallic Li15Si4 phase at the end of the plateau. We have investigated the changes in local structure that occur during the lithiation of Si by ex-situ MAS-NMR. The resonances seen in the discharged electrode spectra were assigned to specific local environments on the basis of the spectra of model intermetallic compounds

in Li-Si system, synthesized as part of this study. The data obtained was compared with the in-situ static SSNMR data of an actual working LIB, which allowed the local structures present in the amorphous phases to be determined and the changes in local structure to be followed. In addition, the in situ NMR method revealed a second process at low voltages, which was not visible by using ex-situ methods. Ex-situ PDF analysis of model intermetallic compounds and Si electrodes stopped at various charged/discharged stages showed changes in Li-Li, Si-Si and Li-Si distances, and could be used to follow the transformation from crystalline to amorphous phases.

FUEL 49

Catalyst structure determination using operando XAFS

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Spectroscopy of catalyst systems under actual operating conditions, or operando spectroscopy, has become instrumental in helping to determine the structures and mechanisms of catalytic systems. Operando spectroscopy is differentiated from in situ spectroscopy in that operando spectroscopy occurs under the actual catalyst operating conditions. In addition, a measure of the catalyst activity is also critical during operando spectroscopy. Operando spectroscopy has revealed that some catalytic systems operate under much different conditions than previously believed based on ex situ analysis. We present some of our recent work using operando XAFS of catalytic systems varying from hydrogen release of hydrogen storage materials to benzene hydrogenation. We present a basic introduction into XAFS and its use as an operando technique and show how this technique can be used to differentiate between catalyst containing highly dispersed nanoparticles and organometallic clusters.

FUEL 50

Examining the correlation between molecular modeling and X-ray scattering structures of Green River oil shale kerogen

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The huge potential for hydrocarbon recovery from oil shale is frequently over shadowed by the difficulties faced in extraction of the bitumen and kerogen from the inorganic shale material in a cost effective and environmentally acceptable manor. While much effort has been expended in developing production technology, details of the kerogen structure are still being explored in order to gain insight into the kerogen/mineral matrix and find more efficient ways to extract the available hydrocarbons.

Two-dimensional models have been proposed that have served as valuable guides to structural detail but one must remember that the resource actually exists in three dimensions. Hence, we have undertaken a molecular modeling effort at the University of Utah that is guided by the SAXS and PDF data obtained on a beam line at the Argonne National Laboratory APS. Comparison of experimental structural data with 3-D modeling (starting with the Siskin structure) provides new insights to the location of various functional groups when the 2-D starting structure is allowed to. The details of the structure are then followed by the energy minimization process that will be discussed.

FUEL 51

In situ characterization of heterogeneous catalysts using time-resolved X-ray diffraction

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Time-resolved X-ray diffraction (TR-XRD) has emerged as a powerful technique for studying the behavior of heterogeneous catalysts in-situ during reaction conditions. (1) In this talk we will review a series of recent TR-XRD studies on water gas shift reaction (WGS) over copper (2) and gold (3) supported on cerium

oxide and Cu and Ni supported on MoO2(4,5). We will also present new WGS studies on CeFe2O4 spinel and ceria supported on copper.

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FUEL 52

In situ XAFS analysis of cobalt-containing fuel cell cathode electrocatalysts

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Oftentimes measuring relevant properties for catalysts must be done in situ. The obvious properties are catalytic activity and selectivity. However, improving catalyst production or discovery may depend on a better understanding of the fundamental structure of the materials under real operating conditions. X-ray absorption fine-structure (XAFS) spectroscopy can be used to probe the atomic and electronic structure of the active electrocatalyst in an operating fuel cell. Specially adapted fuel cell hardware can be used effectively to measure XAFS in situ for transition metal K edges. We present a study of cobalt-containing, non-platinum electrocatalysts that demonstrates the existence of several chemical species under different conditions during the operation of a fuel cell.

FUEL 53

Grazing incidence small-angle X-ray scattering studies of nanometal catalysts

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In the study of catalytic reactions, grazing incidence SAXS (GISAXS) experiments on flat catalytic support substrates with size-selected metal clusters can provide both ex-situ and in-situ information on cluster size, shape, and inter-particle distance (APS beamline 12-ID). GISAXS can also give depth profile information, and the aspect ratio (height/diameter) of a cluster can be calculated from the GISAXS data to obtain the interfacial energy. ASAXS refers to the extension of standard SAXS experiments in which the energy of the probing X-rays is tuned near the absorption edge of an element in the sample which separates the scattering of clusters from that of the support. GISAXS has been used to study the thermal stability and reactivity of Pt and Ag nanoclusters deposited on a variety of surfaces. One example is the partial oxidation of olefins to alkyl oxides where it has been found that the size and shape of catalytic size-selected nanoparticles is important.

FUEL 54

Catalysts important in the refining of Fischer-Tropsch syncrude to fuels

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The properties of Fischer-Tropsch syncrude that influence fuels refining the most are the high olefin and oxygenate content, as well as the high proportion of linear hydrocarbons. Four catalyst types were identified as key catalysts for the refining of Fischer-Tropsch syncrude to on-specification transportation fuels, namely: alumina, solid phosphoric acid (SPA), non-acidic Pt/L-zeolite and mildly acidic Pt/SiO2-Al2O3. Hydrotreating catalysts are also important in Fischer-Tropsch refining, but there is not a single type of catalyst that can be highlighted as being uniquely suited for the hydrotreating of Fischer-Tropsch syncrude. Some generally desirable catalyst attributes for Fischer-Tropsch refining are: non-sulphided (e.g. noble metal), mild acidity and water tolerance.

FUEL 55

Overview of Fischer-Tropsch aqueous product refining strategies

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The production of hydrocarbons from synthesis gas by the Fischer-Tropsch (FT) process is accompanied by the production of water and oxygenates. During the stepwise condensation of the Fischer-Tropsch product, the polar, short chain oxygenates preferentially dissolve in the reaction water to form an aqueous solution. Since the organic products in the aqueous stream constitute up to 10% of the total FT product, there is an economic incentive to refine these compounds. The dissolved oxygenates can either be recovered as chemicals or converted into transportation fuels. This paper provides an overview of the refining strategies that have been considered for the processing of Fischer-Tropsch aqueous products. Refining strategies that will be discussed include: (a) extraction and purification into pure components to be sold as chemicals and solvents, (b) partial hydrogenation of the carbonyls to alcohols, (c) partial hydrogenation followed by dehydration, and (d) conversion of the oxygenates by acid catalysts.

FUEL 56

Blending performance of hydroprocessed coal pyrolysis products in low-temperature Fischer-Tropsch diesel

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Hydroprocessed coal pyrolysis products formed during fixed bed dry bottom coal gasification has been used as blending components in Fischer-Tropsch fuel since the 1980's at Sasol's Synfuels high-temperature Fischer-Tropsch (HTFT) refinery in Secunda, South Africa. The integration of hydroprocessed coal tar (creosote) diesel with low-temperature Fischer-Tropsch (LTFT) distillate in coal-to-liquid (CTL) applications is of industrial importance since it provides a way to produce a final LTFT CTL diesel blend conforming to current fuel density specifications. LTFT distillate, obtained through sulphided base-metal or noble-metal promoted silica-alumina catalysts, has a high cetane number, almost zero sulphur and aromatic content, and a low diesel density. These fuel properties lend LTFT distillate to be used as a blending component to upgrade low quality diesel, for example, creosote diesel, to increase diesel production volumes while meeting stringent exhaust emission regulations. The highly aromatic creosote diesel improves the materials compatibility of the LTFT CTL diesel blends.

FUEL 57

Catalytic oxidative desulfurization of jet fuel for fuel cell applications

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Sulfur compounds contained in petroleum fuels pose an environmental threat. Sulfur content of jet fuel prevents its use for reformer/fuel cell power supplies. We find that ultrasound promotes catalytic oxidative desulfurization (ODS) of jet fuel using activated carbon/formic acid as the catalyst and hydrogen peroxide as the oxidant. When coupled with an effective polishing step, overall sulfur removal performance was about 90%. Reactive chromatography reveals that residual sulfur content is equally divided between un-reacted benzothiophenes and un-extracted sulfides/disulfides and/or benzothiophenes. We find that a wood-based activated carbon catalyst is more effective than a peat-based carbon, and that an ammonium persulfate acid treatment does not boost activity significantly. Dibenzothiophene compounds are more readily oxidized than benzothiophene compounds, and we observe >99% oxidation efficiency of several model DBT compounds using MW 99-R-06 as the catalyst. For the model benzothiophene compounds tested (BT, 2-MBT, and 5-MBT) methyl substitution does not affect reactivity strongly.

FUEL 58

WITHDRAWN

FUEL 59

Catalytic conversion of syngas to oxygenates: Challenges for selectivity and activity

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The conversion of syngas to liquid fuels is of increasing interest since these fuels can be used to supplement conventional petroleum-based fuels. Syngas can be readily produced by thermochemical routes from coal, biomass, and natural gas. In addition to Fischer Tropsch synthesis of hydrocarbons, the catalytic conversion of syngas to oxygenates offers an alternative to biochemical routes to produce ethanol and other higher alcohols. These oxygenates find a number of end uses, such as fuel additives, hydrogen carriers, and chemical intermediates.

Current catalysts typically show high selectivities to C1 products (mainly methane, the most thermodynamically favored product) and relatively low overall CO conversions. Using novel catalyst preparation processes such as liquid phase displacement of nanoparticles and electrodeposition (as well as conventional methods), the C1 selectivity can be limited and the yield of higher oxygenates optimized. Experimental results suggest that the optimum catalyst is one that balances CO insertion and CO dissociation, together with hydrogenation, and that the mechanism is primarily chain growth.

FUEL 60

In situ FT-IR studies of CO and CO2 hydrogenation over titania supported Rh and Rh-Li catalysts

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The conversion of coal-derived synthesis gas into ethanol provides a unique opportunity to develop an affordable and readily reformable hydrogen carrier that can be distributed and stored using the nation's existing infrastructure. One of the challenges is that the catalysts investigated to date suffer from poor overall yields even in cases where the selectivity is reasonably high. A key technical issue in the ethanol production reaction is to keep a high selectivity to ethanol without formation of methane.1,2 Rh-based catalysts are the most widely studied catalyst for hydrogenation of CO to oxygenate compounds and promoters can be used to increase conversion and to inhibit the methanation pathway.1 However, little is known on the reasons as to why the promoters affect the activity and CO bond

cleavage. Therefore it is our goal to investigate the effect of promoters on the reaction pathways. More specifically, we examined the effects of Li on the properties of Rh/TiO2 for CO and CO2 hydrogenation by using in-situ infrared spectroscopy in a transient reactor at ambient pressure and elevated temperatures. The goal is to identify the mechanistic factors that govern the reaction pathway, such as CO adsorption states, CO bond breaking, and the selectivity to methane vs alcohol. The in-situ surface spectroscopy experiments revealed that the presence of the Li promoter does not seem to alter the electronic structure of Rh, but rather it may introduce structural changes that could alter the Rh dispersion and/or bonding with CO.

FUEL 61

Effect of CO2 on CO hydrogenation to ethanol over Rh-Mn-Li/TiO2 vs. Rh-Mn-Li-Fe/TiO2

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We have synthesized multipromoted Rh/TiO_2 to explore how different promoters modify the effects of CO_2 on CO hydrogenation. On Rh-Mn-Li/TiO_2, the addition of the CO_2 to the feed during CO hydrogenation reaction increases methanation and reduces oxygenate formation, consistent with the observation that CO_2 is more easily hydrogenated to methane than CO at the same reaction conditions. Despite increased methanation as a result of the addition of CO_2 to the feed, Rh-Mn-Li-Fe/TiO_2 catalysts produced ethanol at a higher selectivity during the hydrogenation of a CO/CO_2 mixture than for the hydrogenation of only CO. The Fe promoter is believed to increased reverse WGS reaction upon CO_2 addition, resulting in increased CO and decreased hydrogen species on the surface, leading to higher CO insertion activity than when Fe is not a promoter. The result is a higher increase in ethanol selectivity than in methanation activity, causing the EtOH/CH_4 to increase.

FUEL 62

Methane hydrates and global climate change: A status report

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State-of-the-art studies of gas hydrate-climate connections focus on the impact of past and future climate events on gas hydrates, ocean-atmosphere coupling in

predictive models, identifying methane derived from degassing hydrates, and the critical differences in climate susceptibility between permafrost and marine deposits. Over geologic time, climate change has altered the global distribution and inventory of gas hydrates, and the geologic record contains numerous examples of spatio-temporal associations among climate change events, large-scale submarine slope failures, and gas hydrate occurrences. At the same time, terrestrial and marine data often produce contradictory conclusions about the role of gas hydrates during major warming events. Increasingly, researchers are also questioning whether contemporary climate change processes are causing degassing of some hydrates deposits. Field studies suggest that this process may be underway at high latitudes, a result at odds with models predicting long-term gas hydrate stability under realistic climate change scenarios for the near future.

FUEL 63

Gas hydrate occurrence in marine sediments and volcanic ash of the Andaman Arc: Results from the Indian NGHP Expedition 01, Site 17

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Infrared (IR) imaging and co-located lithology of cores from the Indian NGHP-01 Site-17 in the Andaman Arc indicate preferential occurrence of gas hydrate in ash layers. IR and pore water chloride data show that an average of ~2.5% of pore space is occupied by gas hydrate at this site. Assuming that the hydrate occurrence zone (between ~265 and 600 meters below seafloor) is consistent

over a broad area defined by a regional BSR, the overall gas hydrate abundance is 5.4X106 m3/km2. The IR-pore water chloride correlation has large uncertainty that may be reduced by thermal and chemical modeling of gas hydrate dissociation during core recovery. However, the association of gas hydrates and volcanic ash layers observed at NGHP-01 Site-17 provides further evidence for the role of lithology in gas hydrate distribution. This is key for estimating global gas hydrate abundance and understanding the mechanisms that lead to its formation and destabilization.

FUEL 64

Gas production from methane hydrates

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To test the in-situ heating concept and characterize other production schemes, a 72 liter reactor vessel has been built. 4.45% of hydrate was formed in a sand matrix saturated with de-ionized water at 2.2oC and about 600 psi using 99.97% pure methane gas. During the depressurization experiments, a cooling effect, caused by the endothermic dissociation of hydrates was quantified. The observed system temperature decrease was between 4.0 to 0.8 OC. In addition, a transition regime was identified that was manifested as an increased gas production from 9.5 L/min to 13 L/min within a temperature range of -1.6 to 0.0 oC temperature and pressure range of 330 to 310 psig. Results of multiple heating rates for in-situ dissociation tests also agree, within an order of magnitude, to published model simulations and indicate a low heat flux is preferred to yield the highest efficiency which is consistent with our FEMLAB™ simulations.

FUEL 65

Development and test of innovative technologies for gas hydrate exploration and gas production from hydrate bearing sediments

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The project SUGAR (Submarine Deposits of Gas Hydrates – Exploration, Production and Transportation) aims to produce gas from methane hydrates and to sequester carbon dioxide from power plants and other industrial sources as CO_2 hydrates in sediments. This large-scale project is funded by two federal German ministries and the German industry for an initial period of three years. In the framework of this project new technologies starting from gas hydrate exploration techniques over drilling technologies and innovative gas production methods to CO_2 storage in gas hydrates and gas transportation technologies will be developed and tested. Beside the performance of experiments numerical simulation studies will generate data regarding the methane production and CO_2 sequestration in the natural environment. Reservoir modelling with respect to gas hydrate formation and development of migration pathways complete the project. This contribution will give detailed information about the planned project parts with focus on the production methods.

FUEL 66

Hydrate formation from single-phase aqueous solutions of CO_2 in the presence of bentonite particles

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Experiments are being performed at the National Energy Technology Laboratory to investigate the effect of bentonite on hydrate formation from dissolved gases. Experiments are described in which freely suspended bentonite particles were found to promote the formation of CO_2 hydrate, with the degree of subcooling being reduced by 0.5 to 0.9 K compared to pure water. The effect was slightly larger at lower pressures. The goal of this effort is to provide a better understanding of how to predict hydrate stability and reformation in systems where a gaseous hydrate former is dissolved in the aqueous phase. The information may be useful for improving simulation codes that attempt to model hydrate production and the fate of hydrate under climate change scenarios.

FUEL 67

Thermal conductivity and thermal diffusivity of methane hydrate using a single-sided approach

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The National Energy Technology Laboratory has developed a single-sided approach, modified from the Transient Plane Source technique, where the thermal conductivity and thermal diffusivity can be determined from one measurement with the sensor serving as both the heat source and sensing device. The method is suitable for measuring the thermal properties of samples that may be accessible from only one side. We foresee this being easily adapted for field and in-situ measurements. This approach has proven effective at determining the thermal conductivity of low conductivity materials such as laboratory formed methane hydrate. The application of the approach for obtaining thermal diffusivity values of the methane hydrate gave values that were lower than expected as predicted by finite difference modeling and in comparison to recently published values. Here we present a brief synopsis of the proposed approach that should provide accurate values of the thermal properties of methane hydrate.

FUEL 68

Interaction of CO_2 with coals via SAXS

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Interest in CO_2 storage in coal seams and the prospect of concomitant enhanced coalbed methane (ECBM) recovery has prompted investigations of the interactions of high pressure CO_2 with coals. Here we work we report on time-resolved SAXS studies of swelling/de-swelling of selected Argonne Premium (APCS) and New Zealand coal samples exposed to high pressure CO_2 at ambient temperature. The results are interpreted in terms of a two-phase model of gas-filled voids/pores and a solid coal matrix. It is shown that coal swelling/de-swelling due to dissolution/evaporation of CO_2 produces, respectively, a decrease/increase in scattering intensity, reflective of the disappearance/appearance of the smallest scatterers (i.e., voids/pores), accompanied by a shift of the normalized void/pore distribution to larger scatterers. The swelling/de-swelling process is also hysteretic. The pore-size range where these changes are evident is dependent on the coal type. Consideration of the time behavior of the Porod invariant of the scattering curves

suggests that the solid matrix de-swells primarily *via* Class II diffusion, at least for the Upper Freeport coal sample (APCS-1). Results are also compared for different coal samples.

FUEL 69

S-XANES analysis of sulfur forms in coals and kerogens

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Sulfur X-ray Near Edge Absorption Spectroscopy (S-XANES) is routinely used by to collect information about chemical and thermal sulfur transformations in materials such as coal and kerogens. This technique, used in conjunction with other techniques such as XPS and 13C NMR can be used to gain valuable information about sulfur transformations without altering the samples in the process. [1] S-XANES has been performed over the last few years at the Advanced Photon Source beamline 9-BM, which is optimized for low energies XAFS (below 4 keV) and is unique to the APS facility. An overview of beamline design in the context of sulfur characterization is provided along with analysis methods using spectra from model compounds and selected sulfur data for kerogens and coals taken from the literature.

FUEL 70

Detailed heteroatom speciation in petroleum by high resolution FT-ICR MS

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Detailed characterization of crude oil and its associated fractions is hampered by the wide range of chemical functionalities represented in heteroatoms (specifically N, O, S, and metals (typically Ni and V)). Simple variations in ionization efficiency between the chemical types of heteroatoms can mask or enhance their detection in mass spectrometry. The high resolution and mass accuracy afforded by Fourier Transform Ion Cyclotron Resonance (FT-ICR) mass spectrometry make it uniquely suited for the analysis of complex mixtures. With typical mass accuracies in the 100-300 part per billion range, the technique

allows for the unequivocal assignment of molecular formula for species between 50-600 Dalton based on accurate mass measurement alone. The strengths of FT-ICR MS along with advances in ionization techniques have led to rapid growth in petroleum applications of high resolution mass spectrometry. Here, we describe the latest advances in ionization techniques and chemical derivatization methods coupled with FT-ICR MS to enable the detailed analysis of petroleum samples. Recent advances allow for wider speciation of heteroatom classes without tedious preparatory steps.

FUEL 71

Mass spectral characterization of a VGO

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Petroleum is probably the most complex natural product. Unlike the traditional field of natural products chemistry where only one or at most a few compounds of interest are characterized; to effectively utilize petroleum, it is necessary to understand the entire mixture. This complexity is contributed by the two dimensions, kinds of compounds and the homologous series. Traditional mass spectral methods in petroleum analyses tend to group the homologs. We propose a new perspective of characterizing petroleum from both of dimensions. The crude oil was subjected to distillation to generate a VGO, the VGO sample was separated by polarity into three fractions, saturates, aromatics, and polars. Each of these fractions was analyzed by both EI (electron ionization) GCMS and by field ionization mass spectrometry (FIMS). FIMS provides molecular weight information, from which one can infer structures, but detailed structural information is provided by EI GCMS.

FUEL 72

An improved method for determination of kinetic parameters from constant heating rate TGA oil shale pyrolysis data

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Data regression for isothermal or non-isothermal TGA data traditionally involves linear forms of the rate equation because of the subsequent ease of determining kinetic parameters. Linearization methods involve several approximations and

practical shortcomings that often make it hard to precisely determine Arrhenius rate coefficients. These difficulties stem from sources of error like extrapolating to the intercept to determine the natural log of a normalized value. Subjectivity is also introduced when the final activation energies depend on which data points should be included in the analysis. This paper describes a method to use TGA data from multiple heating rates to determine an activation energy and pre-exponential factor. The method fits both the mass versus time curves as well as the derivative form of the data using an advanced optimization program OptdesX. The method was applied to determine the kinetic coefficients for the pyrolysis of kerogen from pulverized oil shale.

FUEL 73

Fluorous metal organic frameworks

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We have recently discovered new advanced porous material, Fluorous metal-organic frameworks (FMOFs), which show enhanced thermal, light and air stability, superacidity, low surface energy and surface tension, in addition to the excellent optical and electrical properties. This talk will overview some fascinating functional properties of FMOFs:

(1) Isolation and crystallographic characterization of several FMOFs.

(2) Gas adsorption and hysteresis, including N2, O2, H2, CO, CO2 and CH4.

(3) Liquid uptake.

(4) Huge, anisotropic and reversible negative thermal expansion (NTE) and positive thermal expansion (PTE) behaviour.

(5) Breathable function and breathing mimics.

(6) Various polymorphs of Ag-3,5-bis(trifluoromethyl)-1,2,4-triazolate system.

(7) semiconductor properties.

(8) Other promising applications.

FUEL 74

Electrochemical hydrogenation and hydrogen evolution on carbon nanotubes

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Recent experimental work demonstrated that CNT can store more than 6 wt% of hydrogen through almost 100% hydrogenation of CNT by formation of C-H bonds. One of the major obstacles for storing hydrogen on CNT through chemisorption is the high energy barriers associated with the adsorption and desorption of H. In this work we focus on theoretically exploring the electro-chemical pathway of hydrogenation and dehydrogenation of CNT in the hydrogen storage and release processes in energy applications. Results on the hydrogenation of CNT and hydrogen evolution on CNT under various applied potentials will be presented.

FUEL 75

A novel method to prepare activated carbon monolith with high mechanical strength

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In the present work, activated carbon monolith (ACM) has been prepared using powdered activated carbon, tar and KOH. Powdered activated carbon was prepared from petroleum coke by chemical activation with KOH. After that, different portions of this carbon were impregnated with an aqueous solution of KOH. A mixture was produced to form homogeneous dough by blending the impregnated material and coal tar. Then, the dough was extruded into column monoliths. The green monoliths were heated under N2 flow and subsequently washed with distilled water.

The results showed that the use of coal tar as a binder produced decrease in both surface area and pore volume of ACM dramatically. With the impregnation of KOH, the surface area and pore volume of ACM slightly increased, whereas the mechanical strength increased considerably. However, the increase of KOH/Powdered activated carbon mass ratio resulted in higher surface area and lower mechanical strength.

FUEL 76

Facile enrichment of tocopherols by automated flash chromatography

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Tocopherols are fat soluble vitamins with antioxidant activity found in most vegetable oils. Analysis of tocopherols presents a challenge due to their relatively low concentration and chromatographic similarity to the oil matrix.

A single-step method using an automated flash chromatography system is described to remove the tocopherols from the oil matrix that allows easy analysis by HPLC other analytical methods.

FUEL 77

Novel catalysts for transesterification of vegetable oils

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Several different ammonium salts as Bronsted acid catalysts for transesterification of vegetable oils into biodiesel fuel have been investigated. The effect of variations in the anion coordinated to the salt will be presented along with the correlation between pKa of the ammonium salt and catalytic activity. Open atmosphere reactions and microwave reactions are considered and compared for efficiency.

FUEL 78

Polypyrrole and platinum nanocomposite for fuel cell applications

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Polypyrrole (PPy) nanotubes were synthesized by using sacrificial template vanadium pentoxide nanofibers as the templates, yielding nanotubes with the outer diameter 50-70 nm and inner diameter 4-8 nm. Platinum (Pt) nanoparticles were then deposited on the polypyrrole nanotubes by chemical reduction, using formic acid as the reducing agent. The Pt nanoparticles are in the range of 4-20 nm.

The PPy-Pt nanocomposites can be applied as electrode materials to reduce oxygen for fuel cell applications. Even in the presence of methanol, the nanocomposite can reduce oxygen without methanol oxidation crossover, which is highly desired in methanol fuel cell applications.

FUEL 79

Ionic liquids as "green" replacements for hydrazines in bipropellant rocket application

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Environmental and health concerns are becoming more and more pressing in the propellant world. Nevertheless, hydrazine and its methylated derivatives are still the state-of-the-art fuels for bipropellant applications. Most of the problems handling hydrazine and its derivatives are related to their volatility, as they are carcinogenic vapor toxins. For these reasons, it is exceedingly attractive to replace hydrazine with ionic liquids (ILs) which have become paragons of environmental friendliness, green chemistry and low vapor toxicity. Ignition of propellants often constitutes a major hurdle in propellant development. Therefore, discovering an IL which shows hypergolic ignition with common oxidizers represents a major achievement. Hypergolic bipropellants are defined as fuel and oxidizer combinations that, upon contact, chemically react and release enough heat to spontaneously ignite, eliminating the need for an additional ignition source. This also makes them highly reliable for spacecraft and satellites which need to fire their rocket engines hundreds, or even thousands, of times during their lifetime. Most known energetic ILs consist of a heterocyclic cation and an oxygen-carrying anion, and in bipropellant application, the cation would thus largely constitute the fuel. Consequently the positively charged fuel portion is rendered more resistant towards oxidation and this particular charge separation should lead to greater stability along with the other well known

advantages of ILs (low vapor toxicity, consequent of low vapor pressure, etc.). However, this could also be a drawback for propulsion because of the greater expected resistance towards oxidation and resulting difficulty in achieving rapid (< 5ms) hypergolic ignition. Although oxidizer anions contribute to the overall performance (i.e., density and oxygen balance) they do not necessarily help with hypergolic ignition (as an extensively oxidized anion would not be expected to participate in oxidative pre-ignition reactions). A task specific design approach leading to ILs possessing hypergolic properties with commonly used oxidizers described.

FUEL 80

Oxidation characteristics of biodiesel and its blends from vegatable oils under accelerated oxidation conditions

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Biodiesel has been gaining worldwide popularity as an alternative fuel and is typically obtained by transesterification of vegetables oils, animal fats. Biodiesel and its blends with petroleum-based diesel fuel can be used in diesel engines without any significant modification of the engines. The problem of biodiesel is to undergo the oxidative degradation over time, mainly influenced by temperature and oxygen. When it is used by fuel, oxidized products of biodiesel from degradation may cause some problems in engine and injection. Therefore, biodiesel blends (0.5, 1, 3, 5, 10, 20 vol. %) and biodiesels (100 vol. %) were evaluated to recognize oxidation characteristics rapidly at 100 °C under accelerated oxidation conditions. From the analysis of biodiesels and its blends after accelerated oxidation, it was considered that density, kinematic viscosity, and acid number should proportionally increase because those showed increased values as oxidation time. Oxidation products after accelerated oxidation were identified by 1H-NMR, FT-IR, GC, and FT-orbitrap APCI-MS to propose oxidation mechanism. In addition, it was synthesized by Diels-Alder reaction to compare with oxidation products to produce by accelerated oxidation. Especially, a comprehensive analytical method atomic pressure chemical ionization tandem mass spectrometry (APCI-MS/MS) with positive ionization mode has been developed. Structural elucidation of various oxidation products

by accelerated oxidation was carried by CID, HCD and exact mass analysis using FT-Orbitrap Mass Spectrometer. The composition of oxidized biodiesel was changed to decrease unsaturated bond.

FUEL 81

Synthesis and characterization of functionalized mesoporous carbon acid catalyst for biodiesel production

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The current method of biodiesel production using homogenous acid or base catalysts have drawbacks due to the low biodiesel yields for feedstocks with high levels of free fatty acids or moisture, the loss of catalyst, and the need for large volumes of wash water to remove the residual catalyst. Mesoporous carbon acid catalysts for biodiesel production was synthesized by reacting pluronic, phloroglucinol and formaldehyde under controlled conditions followed by thermal treatment at 840 °C and further reaction with fuming sulfuric acid to yield the functionalized the mesoporous carbon. The mesoporous carbon catalysts were characterized using XRD, SEM, TGA, and BET analysis of surface area. Results suggest the presence of mesopores and sulfonic acid groups. The catalytic activity was monitored using the transesterification reaction to yield fatty acid ethyl esters and glycerol-based esters. The emissions of the biofuels were evaluated by GC-MS analysis of the exhaust gases from a generator engine.

FUEL 82

Synthesis of biodiesel components from pure fatty acid and analysis of their fuel characters

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The biodiesel produced by the transesterification of vegetable oils and animal fats is expected to be useful as one of the eco-friendly biomass-based alternatives to petrodiesel. Our research group was studied about analysis of tirglyceride in vegetable oil and FAMEs in biodiesel using high performance liquid

chromatography and gas chromatography in recently. In this study, we synthesized pure biodiesel components from pure fatty acid like myristic acid, palmitic acid, stearic acid, oleic acid, linoleic acid, linolenic acid, arachidic acid, and behenic acid under base catalyst system. These synthesized biodiesel components were analyzed the fuel character such as cetane number, kinematic viscosity, CFPP, cloud point, lubricity, and so on. These physical propertied of biodiesel components have relativity with total fuel character of biodiesel fuel from raw material as mixed tiglycerides.

FUEL 83

Study on the effects of activator on the stability of sulfonated cobalt phthalocyanine in alkaline solution

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In view of coagulation of sulfonated cobalt phthalocyanine in alkaline solution, The effect of adding CCBA or TEAH into the solution of 10% NaOH-100ppmCoPcS was detected. It was revealed that, the addition of TEAH has little effect on the stability of catalyst-alkaline solution. The stability of catalyst-alkaline solution can be improved greatly by adding CTAB. The removal efficiency of octanethiol of four kind of catalyst-alkaline solution was detected, the results revealed that the removal efficiency of octanethiol of adding 0.25%CTAB into catalyst-alkaline solution was much higher than that of catalyst-alkaline solution, when the time was 6min, the removal efficiency were 97.14% and 75.13% respectively.

FUEL 84

Catalytic role of nanostructured carbon on $NaAlH_4$ hydrogen sorption

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A systematic study of the catalytic role of carbon nanostructures on hydrogen release and absorption of $NaAlH_4$ has been conducted with a Sievert's type apparatus. These experimental results were compared with synergistic first-principles *ab initio* molecular dynamics simulations in order to elucidate the origin of catalytic behavior within the NaAlH4 molecule. $NaAlH_4$ interaction with an electronegative substrate such as carbon nanotubes inhibits charge transfer from the Na^+ cation to the alanate unit thereby weakening the Al-H bond. The result is catalytic dehydrogenation at suppressed temperatures as well as reversible absorption of 1.5 – 4.3 wt % H_2 to reform the $NaAlH_4$ material. Carbon fullerence (C_{60}) showed the best catalytic behavior for rehydrogenation.

FUEL 85

Development of a REMPI/SPI-TOFMS for the detection of tar formation in biomass gasification

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Perhaps the most difficult challenges facing the extraction of energy from biomass result from its chemical makeup, about 38-50% cellulose, 23-32% hemicellulose, and 15-25% lignin. The bulk of these biopolymers are carbohydrates (up to 80%) and much of the thermochemistry associated with these materials remains poorly characterized. Initially, pyrolysis decomposes and volatilizes the polysaccharides. In gasification, these products undergo further cracking, which leads to the formation of recalcitrant tars (aromatic compounds). We have developed and REMPI/SPI TOFMS system to monitor simultaneously aromatic compounds (REMPI) and their suspected precursors (SPI) to aid in understanding the mechanisms by which these recalcitrant tars are formed. This poster will describe the instrument in depth and present initial findings using an entrained flow reactor.

FUEL 86

Enzymatic bioreactor for butanol production

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One of the major problems with microbial butanol fermentations is toxicity of solvents to the microbes. Researchers are working on improving the gas-stripping procedure, liquid-liquid extraction, and pervaporation as well as genetically modifying the bacteria into a butanol-tolerant microbes. To eliminate all problems we are proposing an enzymatic bioreactor by which the pyruvate will be enzymatically converted to butanol. Source of pyruvate will come from lignocelluloses from various biomass that will be enzymatically treated to efficiently liberate sugars and convert them into a non-toxic/stable pyruvate intermediate. The proposed bioreactor (butanol dehydrogenaes, butyryl-CoA dehydrogenase, 3-hydroxybutyryl-CoA dehydrogenase) will consists of enzymes/cascade immobilized within the micellar structures of a modified micellar polymer, such as: Nafion®, chitosan, and/or alginate. Our current work focuses on optimal growth factors for Clostridium acetobutylicum ATCC® 824TM to obtain most favorable enzyme isolation and purification procedure yielding highest catalytic activity possible for all three-enzymes. Representative data shows that we were able to detect NAD- and NADP-dependent butanol dehydrogenase activity within the crude extract of the cells with specific activity of 2.44 and 3.53 nanomol/min/mg respectively.

FUEL 87

Factors affecting lignin measurements in dilute acid pretreated herbaceous feedstock

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Determining the lignin content in herbaceous materials before and after dilute sulfuric acid pretreatment is an important element to optimize pretreatment conditions for bioethanol production. Previous research at NREL has found the lignin content determined by the Klason method in pretreated corn stover appears to contain more lignin than could be accounted from the measured lignin content in the untreated material. We investigated the factors affecting lignin measurement in dilute acid pretreated feedstock using combinations of nitrogen analysis, 13C cross polarization/magic-angle spinning (CP/MAS) solid-state nuclear magnetic resonance (NMR) spectroscopy, removal of lignin using acid chlorite bleaching, and 13C-labeled sugars. It was found that remaining protein in acid insoluble residue is 0.5-1.0 wt% of original corn stover and only minimal contamination due to carbohydrate was observed. However, degradation products were present in acid insoluble residue suggesting that low molecular

weight compounds can be condensed on to the biomass substrate after pretreatment.

FUEL 88

Immobilization of the first five glycolysis enzymes for biofuel cell applications

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The aim of this research is to mimic the glycolysis pathway at an anode surface. To immobilize the enzymes on an electrode, the enzymes need to be suspended in a polymer that adheres to the electrode surface. Hydrophobically modified chitosan was studied because chitosan is inexpensive, non-toxic, biodegradable, and biocompatible, unlike other frequently used polymers. Each of the first five enzymes (excluding triose phosphate isomerase) was assayed to see whether modified chitosan membrane is capable of maintaining enzyme activity. A previous study demonstrated the capability of chitosan to effectively immobilize hexokinase. More recently, phosphoglucose isomerase (PGI), phosphofructokinase(PFK), aldolase, and glyceraldehyde-3-phosphate dehydrogenase have been tested. The activity of PFK was testing using chemiluminescent assay. PGI, aldolase, and glyceraldehyde-3-phosphate dehydrogenase activity was tested using UV/Vis spectrophotometry. PGI and PFK maintained activity in the polymer, whereas aldolase activity was minimal. The activity of glyceraldehyde-3-phosphate dehydrogenase was significantly decreased.

FUEL 89

Methanol biofuel cell based on NAD-dependent enzymes immobilized at electrodes by hydrophobically modified Nafion

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In this study, we employed micellar polymeric encapsulation techniques in developing a methanol/air biofuel cell through the combined immobilization of NAD+-dependent alcohol dehydrogenase, aldehyde dehydrogenase and formate dehydrogenase within a tetrabutylammonium bromide (TBAB) modified Nafion to oxidize methanol to carbon dioxide with poly(methylene green) acting as the mediator electrocatalyst electropolymerized on the surface of the carbon paper electrode. The methanol biofuel cell resulted in a maximum power density of

98.8±7.65ìWcm-2 and an open circuit potential of 0.82±0.01V, which is a 4.26 fold increase in power density and a 5.6 fold increase in current density.

FUEL 90

Optimization of PQQ-dependent alcohol dehydrogenase activity in Gluconobacter sp. 33 for use in biofuel cells

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Biofuel cells convert energy obtained from biochemical reactions into electrical energy by the use of biological catalysts. The enzyme's ability to catalyze various reactions enables the biofuel cell to use a wider range of substrates as fuels, such as alcohols, sugars, and fats, to produces electrical energy instead of sources that are limited, such as oil. It is an advantage to use PQQ-ADH over NAD-ADH in order to extend the lifetime of the ethanol biofuel cell and allow for direct electron transfer. In order to increase the activity of PQQ-dependent ADH, ethanol was introduced to the growth media for Gluconobacter sp.33. Also, the pH of the media was altered to 6.0 and 6.5 in order to see the effects of the pH of growth media on the enzyme activity. Addition of ethanol to cultivation media and optimization of the pH may be the beginning of improvement of PQQ-ADH activity which in turn will allow the fabrication of higher power output ethanol biofuel cells.

FUEL 91

Performance of PEG membranes in scale-up of pervaporation for gasoline desulphurization

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Environmental concerns have resulted in legislation which places limits on the sulfur content of gasoline. Considering the disadvantages of traditional hydrotreating technology, it is necessary to develop more efficient and economical sulfur removal way. Gasoline desulphurization by membrane process is newly emerged technology, which has provided an efficient new approach for the sulfur removal and gained increasing attention of membrane and petrochemical field. In this study, scale-up experiments of pervaporation (PV) for gasoline desulphurization have been conducted. The aim of this study was to investigate the process and performance including the influence of operating parameters, desulphurization performance, octane number, and design

considerations. It has been demonstrated that the sulfur content of FCC gasoline was reduced from 750¦Ìg/g to 70¦Ìg/g, when the retentate rate was above 70% (Fig.1).

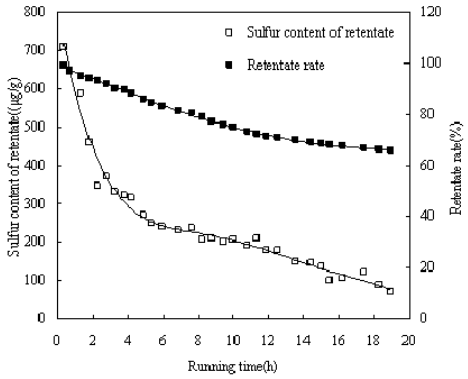

Fig. 1. The changes of retentate rate and sulfur content of retentate with running time

Octane number has attracted more attention for gasoline desulphurization technology. Whether or not there is octane number loss for desulphurization process with PEG membranes is a necessary investigation from economic considerations. According to above GC hydrocarbon group analysis, the octane numbers of retentate stream were a little higher than those of feed. However, the octane numbers for feed, retentate stream and permeate products changed little as a whole (Table 1).

Table 1 Octane numbers for feed gasoline, retentate and permeate samples

Feed gasoline		Retentate sample		Permeate sample	
RON	MON	RON	MON	RON	MON
90.8	77.9	92.0	78.9	90.3	77.5

FUEL 92

Poly(arylene ether)s carrying pendant (3-sulfonated)phenyl sulfonyl groups

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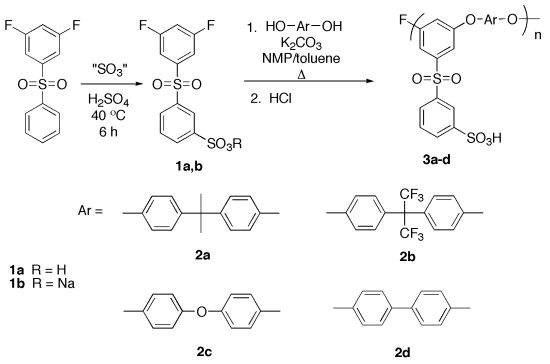
A series of new sulfonated poly (arylene ether)s containing one sulfonic acid group, located on a pendant phenyl sulfonyl moiety, at every repeat unit was synthesized using 3, 5-difluorophenyl sulfone, **1**, and a variety of bisphenols. A

conventional nucleophilic aromatic substitution (NAS) process was utilized for the homopolymerization/ copolymerization. Polymerization reactions of **1** in NMP at 180 °C provided the corresponding linear sulfonated poly (arylene ether)s, s-PAEs, with number average molecular weight, M_n, ranging from 10,300 to 15,700 Daltons. All of the polymers were characterized by ^{1}H and ^{13}C NMR spectroscopy, thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC). All of the samples possessed excellent thermal stability. The polymer samples also formed tough peelable films when DMSO solutions were slowly evaporated on a glass slide.



FUEL 93

Producing energy efficient concrete using Illinois coal fly ash

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Autoclaved aerated concrete (AAC) is a lightweight, energy-efficient, fire-retardant construction material which is used widely in Europe. Conventional AAC is produced with ground sand as the major ingredient. However, with adequate blending, AAC can be made with fly ash, a coal combustion waste material, as a substitute for ground sand. This study conducted bench-scale tests making AAC with Class F fly ash from four different sources in Illinois. AAC blocks were successfully produced to contain fly ash between 60 to 66 percent by weight. The evaluation tests indicated that their engineering properties, including density and compressive strength met ASTM C1386 specifications for AAC wall construction units. Producing AAC using fly ash could add value to this coal combustion waste product and reduce the disposal burden to the power generation companies burning Illinois coals.

FUEL 94

Pyrolysis of lignin model compounds using a hyperthermal nozzle: Decomposition pathways of the aryl ethers

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We have studied the pyrolysis of anisole, guaiacol and syringol, possessing the characteristic aryl ethers linkages ubiquitous in lignin, a major constituent of biomass. The thermochemical conversion of biomass into liquid fuel is complicated by the production of tars during gasification process. The key in improving the efficiency of biomass thermochemical conversion techniques lies in the fundamental understanding of reaction mechanisms. In this study we are investigating the effect of substituents on the decomposition pathway of anisole, and also the reaction pathways leading to aromatic formations. We have used single-photon ionization time-of-flight mass spectrometry to identify the intermediates in these reaction mechanisms. These provide valuable insight into the primary reaction pathways followed during biomass thermal decomposition. Products from these reactions are aromatic molecules and radicals. We calculated the relative energy differences between reactant, transition states, and products using the CBS method.

FUEL 95

Surface modification for efficiency improvement of inline solar cell manufacture

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Inline processing, one of the fastest-growing production processes for crystalline silicon solar cells, uses continuously operated belt furnaces to achieve higher overall throughput compared with traditional batch processing. A second, major advantage of inline processing - improved manufacturing yields through reduced breakage of today's thinner, increasingly delicate wafers - is accomplished by eliminating several handling steps unique to batch processing techniques. This paper describes the influence of ECN-Clean, developed by Mallinckrodt Baker

and ECN, whose application increases the efficiency of solar cells produced using inline processing by approximately 0.3 percent absolute, compared with standard inline processing. This increase is achieved by using a wet chemical surface modifier after emitter formation. Additionally, we present experimental data on establishing a stable process on an industrial scale, prior to optimization of the line for cell efficiency.

FUEL 96

Tar quantification from a fluidized bed biomass gasification: Gas chromatographic and gravimetric methods

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In this paper, tar produced from a bench scale (1kg fuel/h) fluidized bed biomass gasifier was collected and analyzed by gas chromatographic and gravimetric methods. Both methods were performed to evaluate tar speciation and yields. Gas chromatographic method identified 13 compounds in raw product gas, principally "lighter tar" species at an average concentration of 15.5 g m-3 dry gas. Gravimetric methods found "heavier tar" components present at 5.3 g m-3 of dry gas. Tar fractions identified by the two methods were not mutually exclusive, but can be used to supplement one another. Tars conversions were accomplished using nickel catalysts.

FUEL 97

A comparative study of ZnO-CuO-Al2O3 /SiO2-Al2O3 composite and hybrid catalysts for direct synthesis of dimethyl ether from syngas

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Dimethyl ether (DME) has garnered considerable worldwide attention as a clean and environmentally benign fuel and a feedstock for production of petrochemicals and various other hydrocarbon fuels. In this work, two different strategies for the preparation of active dimethyl ether catalysts are evaluated using CuO-ZnO-

Al2O3 and SiO2-Al2O3 as methanol synthesis and methanol dehydration catalysts components, respectively. Composite catalysts are prepared by mixing of the two freshly precipitated catalyst precursors and by co-precipitation methods whereas hybrid catalysts are prepared by mechanical mixing of the two calcined catalyst components by grinding. Composite catalysts are partially deactivated during the catalyst preparation or calcination stages and therefore exhibit much lower activity as compared to the hybrid catalysts towards syngas conversions.

FUEL 98

Adsorbate Cu interactions and catalyst morphologies under reactive water gas shift environment: A first principle study

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The water gas shift reactions (WGS) are widely used in several industrial processes and are catalyzed by Cu catalysts. WGS is used to produce high purity hydrogen and the reverse reaction (RWGS) is essential for upgrading CO_2 to CO. In many fossil fuel derived CO_2 feedstocks, there are sulfur (S) impurities which can adsorb on the Cu surfaces and block the active sites of the catalyst for the desired reaction and can result in catalyst deactivation. However, there is hydrogen pressure which can destabilize the adsorbed S by forming H_2S that may desorb from the catalyst surface. The extent of destabilization depends on the chemical potentials of the species which are determined by reaction conditions. Moreover, occupancy of the active sites could also caused by the presence of other possible adsorbates such as CO and O. To determine the interactions between possible adsorbates with Cu catalyst, the adsorption properties of these different adsorbates on low Miller index facets of Cu surfaces were studied considering the thermodynamic equilibrium of facets with the reactive environment. The aim of this work is to combine atomistic thermodynamics with a computational approach (DFT) to understand the structure and stability of different adsorbate poisoned Cu catalysts that are in equilibrium with their environment and to investigate the effect of hydrogen gas in destabilizing the possible adsorbates. The adsorbate phase diagrams on each surface were constructed as a function of corresponding chemical potentials which showed S poisoning occurs even at ppm levels of H_2S in the environment. We found out that the presence of hydrogen pressure can be utilized to regenerate poisoned slabs at high temperatures. The shapes of a Cu nanoparticle under to various experimental conditions were determined using the Wulff construction which points out significant change in catalyst morphologies under reactive environment conditions.

FUEL 99

Catalytic strategies for upgrading of fuels from conventional and renewable resources

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The combination of Quantitative Structure Property Relationships (QSPR) with model compound studies provides great potential for optimizing catalytic strategies for fuel upgrading. Through this approach, QSPR models are utilized to predict fuel properties of interest for model compounds as well as any potential reaction products. Combined with QSPR, catalytic studies are performed of model compounds, while attempting to maximize selectivity to products with the maximum predicted fuel properties of interest. Through this approach, QSPR provides the direction to which types of bonds should be broken or formed to maximize fuel properties, while model compound studies relate the properties of the catalyst and reaction conditions to form specific products. The end result is a guided approach to catalyst design which maximizes knowledge gained, with a constant link to practical application through fuel property prediction. As the process progresses, practical advancements are gained in leaps and bounds towards the desired result as the resulting strategy will have a firm footing on the fundamental relationships between the molecules and the catalyst. In this contribution, examples will be given for the development of important fuel properties, their prediction with QSPR, and further optimization through model compound studies. Transitioning of these strategies to oxygenated hydrocarbons more representative of renewable fuel sources will then be discussed.

FUEL 100

Characterizing and designing bimetallic catalysts for selective reductions of oxygenates

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Design of catalysts for selective reduction of carbohydrates is an important objective for development of biorefining processes. Bimetallic catalysts of tailored composition offer promise, for example, in reactions where it is desired to selectively hydrogenate a C=C function in the presence of an oxygenate function. The reactivity, electronic structure, and chemical properties of bimetallic catalysts prepared by electroless deposition (ED) have been studied using a combination of reaction studies, surface spectroscopies, and density functional theory (DFT) calculations. Comparisons between experiment and theory were used to identify the most active catalyst structures and to elucidate the mechanism for the higher activity and selectivity of ED-prepared Ag-Pt/SiO2 catalysts (compared to Pt/SiO2 catalysts) for C=C hydrogenation of 1-epoxy-3-butene to 1-epoxybutane. The suggested mechanism is consistent with electronic (ligand) and bifunctional effects leading to enhanced catalytic performance.

FUEL 101

Key catalysis of metal cation-exchanged ZSM-5 zeolites for conversion of methane in the presence of ethene

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We have found that Ag^+-exchanged zeolites are catalytically active for methane conversion in the presence of alkenes (ethene or propene) under non-oxidative conditions at temperatures (~650 K) much lower than those required for oxidative methane coupling. If highly polarized methoxy groups ($ZO^{\delta-}$ $CH_3^{\delta+}$) are formed in addition to the metal-hydride species $[M–H]^{(n-1)+}$, as in the case of Ag^+-exchanged zeolites, the conversion of methane will also proceed over zeolites exchanged with metals other than silver in the presence of C_2H_4.

In this study, the development of a new activation method for methane conversion over metal cation-exchanged zeolites is foucused. Furthermore, the reaction mechanisms for methane activation and the formation of various hydrocarbons, i.e. propene, benzene, and toluene, are also proposed.

FUEL 102

Mechanistic insights into dimethyl ether homologation to branched hydrocarbons on acidic zeolites

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We report here the selective conversion of dimethyl ether (DME) to 2,2,3-trimethylbutane (triptane), an alkane with high octane number, and isobutane on acidic zeolites at modest temperatures (400-500 K) and pressures (60-250 kPa). Homologation preferentially forms C4 and C7 alkanes (40% and 30% C-selectivity, respectively). Isobutane accounts for 90% of C4 hydrocarbons and triptane for 80% of C7 products. Alkene-DME isotopic and kinetic data were used to measure methylation, hydrogen transfer, and isomerization rates and to probe chain growth with unprecedented detail. This triptane and isobutane specificity, previously unreported on solid acids, reflects a positional preference for methylation among growing chains, leading to backbone structures that cannot readily undergo scission or methyl shift. Co-homologation of DME with alkenes or alkanes also occurs with selective formation of isobutane and triptane and at higher rates than for DME reactants. Alkane co-homologation requires adamantane as a hydride transfer co-catalyst and allows the upgrading of low-value alkanes, which provide the H-atoms required in homologation of oxygen-rich feedstocks without concurrent carbon rejection as unsaturated byproducts.

FUEL 103

Solid phosphoric acid: Have the sands of time run out for this steadfast catalyst?

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Solid phosphoric acid (SPA) is one of the key catalyst types employed for the conversion of Fischer-Tropsch syncrude to transportation fuels. Advances in the chemistry, catalysis and application of SPA for olefin oligomerization, aromatic alkylation and olefin hydration is reviewed. SPA catalysts have a small environmental footprint and provide significant refining flexibility. It can be used to produce high-octane olefinic motor-gasoline, alkylate quality paraffinic motor-gasoline, jet fuel and it can also be employed to reduce refinery benzene. In most instances reference is made to the commercial performance of SPA, including the specific behaviour of SPA with respect to Fischer-Tropsch olefins and oxygenates.

FUEL 104

Transition-metal-based catalytic systems for the dehydrogenation and metathesis of alkanes: Solution-phase and solid-supported iridium-based pincer catalysts

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Tandem catalyst systems, comprising pincer-ligated iridium-based catalysts for alkane dehydrogenation and catalysts for olefin metathesis, have been found to effect the overall catalytic disproportionation/metathesis of *n*-alkanes to give exclusively *n*-alkane products. Under some conditions (but not generally) selectivity is obtained for C(2n-2) alkane plus ethane from 2 mol C(n) alkane. Mechanistic and computational investigations have addressed issues of rates and selectivity. Systems comprising soluble and heterogeneous catalysts will be discussed. Significant progress has been made toward the development of systems with supported pincer complexes; in some cases the supported systems afford longer lifetimes and rates comparable to or even greater than their solution phase analogues.

FUEL 105

State-of-the-art perspectives of natural gas hydrates in industrial flow assurance

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An overview of the industrial relevance and consequences of hydrates in flow assurance (maintaining flow in wells, networks, and pipelines) will be presented. Blockage of wells, networks and flow lines with Hydrates is a crucial area of study for flow assurance. This takes place in the evaluation of the risk involved and design of processes to produce oil and gas reservoirs. This problem has been credited as an order of magnitude more important than any other in posing a threat to resource production.

Current perspectives of advanced hydrate technologies that could be applied to manage hydrate formation in flowlines are discussed, including the use of kinetic hydrate inhibitors, and production without chemicals. Advancement of these

hydrate technologies requires fundamental understanding of water-hydrocarbon interfacial phenomena, multiphase flow of resources with fluids containing hydrates, and the development flow simulation tools that reflect the various methods by which hydrates can block flow.

FUEL 106

Interpretation and modeling of chord length distribution from FBRM results during gas hydrate formation and agglomeration from water-in-oil emulsion

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Gas hydrates formation during the production of crude oil from water in oil emulsion is of particular interest. Once hydrates form in the pipeline, individual gas hydrate particles agglomerate together and form a plug preventing fluid flow. Therefore, an understanding of the particle size during the crystallization process is necessary. This work presents hydrate formation and agglomeration in flow loop using a Focused Beam Reflectance Measurement (FBRM) probe for in situ particle size analysis. The FBRM provides a quantitative Chord Length Distribution (CLD) during the crystallization process of water-in-oil emulsions into gas hydrate slurries. In order to better interpret the CLD measurements, a modelling work has been made. The agglomerates are considered as fractal objects composed from a polydisperse spherical population of particle. A simulation of the CLD of random aggregates characterized by various fractal parameters is performed in order to interpreter the CLD of the aggregates.

FUEL 107

Managing gas hydrates at high water cuts with antiagglomerant

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Gas hydrate blockages pose an outstanding flow assurance challenge for hydrocarbon production with high watercuts because hydrate inhibition with thermodynamic inhibitors like methanol often becomes economically unfeasible. Some production wells can be pre-maturely terminated due to risks of hydrate blockages because subcooling in deepwater production is generally too high for kinetic hydrate inhibitors (KHI's) to be effective and it is commonly believed that

anti-agglomerant hydrate inhibitors (AAHI's) are not designed to work for watercuts higher than 50%. To demonstrate the feasibility and principles for managing gas hydrate risks at high watercuts with AAHI's, systematic hydrate laboratory testing at various watercuts was conducted on a Rocking Cell apparatus. Results showed that the ability of AAHI to prevent hydrate blockages at high watercuts strongly depend on the brine salinity. Even though a small increase in the salinity does not shift the hydrate phase diagram by much, it can cause a step change in the performance of AAHI at high watercut. It was also revealed that when a thermodynamic hydrate inhibitor like methanol is mandatory, a small dosage of AAHI in combination with methanol can significantly reduce the amount of methanol required.

FUEL 108

Studies of mass transfer resistances to hydrate formation

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Hydrate films typically form at gas-water interfaces where the concentrations of guest and host molecules are the highest. Once formed, the films provide a significant mass transfer barrier to further hydrate formation. However, there is some controversy about whether it is the transport of the guest or the host molecule that controls further hydrate growth.

In this article, methane hydrate films were formed at a gas-water interface and the gas phase was replaced by a partially deuterated methane molecule (CD3H). The concentration profile of this tracer molecule across the hydrate films was studied over time using confocal Raman spectroscopy. The films were found to contain gas-filled pores which provided pathways for gas migration. These pores annealed over time, increasing the mass transfer resistance. The concentration of CD3H in the hydrate phase was much lower than in the gas phase, suggesting a slow rate of hydrate formation within the film.

FUEL 109

Enhanced rate of gas hydrate formation in a silica sand matrix compared to a stirred vessel

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Hydrate formation experiments were conducted for two single gas and three gas mixtures. These systems are relevant to technologies under development for natural gas hydrate storage and transportation and for CO2 capture and sequestration. CH4/water, CH4 (90.5%)/C3H8 (9.5%)/water and CH4 (91%)/C2H6 (9%)/water are the hydrocarbon systems. CO2/water and CO2 (38.1%)/H2 (59.4%)/C3H8 (2.5%)/water are the systems studied for CO2 capture and sequestration. Two types of experiments were conducted for the above systems. One was conducted by dispersing water in silica sand, while the other in a stirred tank vessel. Both types of experiments were conducted at a constant temperature and in a closed system having the same experimental pressure at the start of the experiment. The presence of silica sand was found to enhance the kinetics of hydrate formation significantly and there by resulting in a higher percent of water conversion to hydrates in lesser time for all the systems studied.

FUEL 110

Progress on the gas hydrate process for CO2/N2 and CO2/H2 separation using a large scale apparatus

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One of the new approaches under consideration for the capture of CO2 from treated flue gas from a conventional power plant and fuel gas from an integrated gasification combined cycle power plant is through gas hydrate crystallization. In this work we report the progress towards the demonstration of the hydrate-based process for post and pre-combustion capture of capture of CO2 in a new large scale apparatus. Gas hydrates were formed with CO2/N2 gas mixture containing 16.9 mol % CO2 and rest N2 in the presence of 1.0 mol% tetrahydrofuran. The gas uptake was significantly higher in the new apparatus on a water free basis which was achieved due to better gas/water contact. Moreover, the CO2 recovery was found to be 0.63 compared to 0.46 indicating a better separation of CO2 from the feed gas. Our results successfully demonstrated that it is possible to scale up the hydrate based separation process for CO2 capture.

FUEL 111

Uncertainty analysis of gas hydrate gas handling applications

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This presentation will develop the relationship between technical knowledge and uncertainty and application for gas handling technologies. Hydrate gas processing can be described by three major stages: formation, separation, and dissociation. The most generic processing operation are separation, storage, and transport. These are distinguished from each other by nuances that arise from addressing the risks associated with each stage and the product requirement. While research has strongly focused on formation processes, the other steps are equally important in innovating a hydrate gas processing operation.

FUEL 112

Application of Raoult's Law to model contaminant mixtures of polycyclic aromatic hydrocarbons

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The by-products of incomplete combustion and other fuels processing abound with complex mixtures of polycyclic aromatic hydrocarbons (PAH). The fate and transport of PAH mixtures in the environment are largely governed by their vapor pressures, yet these fundamental data are often unavailable. We employ the Knudsen effusion technique to measure the vapor pressures of several multi-component PAH mixtures of constituents often found in the soils of former manufactured gas plants (MGPs). We compare experimental vapor pressure results to Raoult's law to establish the applicability of this idealized approximation of vapor pressure behavior to high molecular weight mixtures. Finally, we present vapor pressure measurements on contaminated soil from a former MGP. The results show that Raoult's law is a reasonable approximation to model the vapor pressures of the high molecular weight fractions in PAH-contaminated soil.

FUEL 113

Characterization of aircraft gas turbine engine particle emissions

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Aircraft emissions are a small but growing contribution to the overall emissions problem. Recent advances in measuring the quantity, size, and composition of aircraft particle emissions should improve predictions of potential human health and environmental impacts. Soot is the major contributor to particle mass emissions, and different engine technologies exhibit distinct relationships between EIm-soot and power. The total number of particles emitted (EIn-total) is controlled by fuel sulfur content, and sulfuric acid appears to be the primary driver for new particle formation. Sulfate and organic material are the primary components of volatile particle mass. Nucleation/growth mode particles formed at idle may be dominated by organic material. Layers of volatile material coated on soot particles at take-off conditions may contain roughly equal parts organic and sulfate material. Organic particle material has two primary contributions: products of incomplete combustion and lubrication oil.

FUEL 114

Control of flue gas mercury emissions: Effects of acid gases on sorbent reactivity

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Flue gas–mercury interactions on the carbon surface are extremely important in determining the effectiveness of injected carbons for mercury control in coal combustion. The role of acid gases promoting the reactivity of activated carbon for mercury capture is elucidated in this paper. Parametric tests were conducted with thin beds of carbon sorbent at several concentrations of HCl, SO_2, and NO_2. Low concentrations of HCl (0–5 ppm) in flue gas typically result in an induction period, where capture of mercury is initially lower but then increases after about 30 minutes of exposure. High concentrations of NO_2 are able to overcome the induction when the HCl is 5 ppm, but not when it is 0–1 ppm. The results are consistent with a model where HCl and NO_2 react with a basic carbon surface to generate a cationic center which is an active catalytic site for mercury oxidation.

FUEL 115

Detailed microphysical modeling of particle emissions from aircraft gas turbine engines

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Particulate matter (PM) emissions from aircraft engines have received increased attention due to their impacts on climate, health, and regional air quality. However, understanding of PM formation from aircraft emissions at ground level is still limited. In this talk, a detailed, one-dimensional model consisting of plume chemistry, wake dilution and aerosol microphysics is presented to study PM formation from aircraft engines. Parametric studies were performed to study different sampling setups in recent field measurement campaigns. Our results show that two competing particle formation mechanisms are present: formation of new particles via nucleation and coating onto existing particles via condensation. Our results also suggest that nucleation is mainly controlled by ambient properties (temperature and relative humidity), whereas condensation is dependent on engine power. A comparison of our modeling results with experimental data suggests that the important physics are being captured, and the model may be used to interpret experimental results and help guide future directions of field measurements.

FUEL 116

Fate of arsenic and selenium in air pollution control devices in coal-fires power plants

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The behavior of arsenic and selenium in coal-fired power plants is reviewed in this paper with the intent of showing the pathways by which these elements leave the coal-fired boiler and the coal and operational factors that affect the partitioning of these elements among the output streams.

FUEL 117

Potential of animal waste as a reburn fuel on emissions control: Performance

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A reburn process is used in boilers to reduce NOx. Instead of firing natural gas (NG) as a rebun fuel, cattle biomass (CB) has been proposed as a renewable, supplementary fuel for reburning with coal. Reburning CB with coals has the potential to reduce NOx and Hg emissions in coal-fired boilers as well as to reduce fuel costs, lower coal consumption, decrease nonrenewable CO2 emissions, and dispose of burdensome agricultural waste from large concentrated animal feeding operations (CAFOs). The goal of this study is to determine conditions for the best NOx reduction using blends of CB and coal as reburn fuels. The effects of reburn fuel type and equivalence ratio (ER) were investigated. The effects of high ash in CB on the performance were also investigated. NOx reductions increased with an increase of the ER in the reburn zone and resulted in 96% and 93% NOx reductions when reburning with dairy biomass (DB) and feedlot biomass (FB), respectively. The results presented CB (both DB and FB) can be used a very effective reburn fuel for the NOx emission control in coal-fired power plants. The burnt fraction (BF) increased with the increase of the proportion of CB in reburn fuels. The results of ash fusion temperatures (AFTs) indicated that the ash deposited during CB combustion was more difficult to remove than the ash deposited during coal combustion.

FUEL 118

Soot deposit properties in practical flames

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A laboratory-scale device (water-cooled deposition probe) was designed for studying soot deposition in a laminar ethylene-air premixed flame. This experimental tool facilitates the evaluation of the deposition rates and deposit characteristics such as deposit thickness, bulk density, PAH content, deposit morphology and thermal properties, under both water-cooled and uncooled conditions.

Additionally, a non-intrusive Laser Flash Technique was used to estimate experimental thermal conductivity values for soot deposits as a function of

deposition temperature (water-cooled and uncooled experiments), location within the flame and chemical characteristics of the deposits.

Important differences between water-cooled and uncooled surfaces were observed. Thermophoresis dominated the soot deposition process and enhanced higher deposition rates for the water-cooled experiments. Cooler surface temperatures resulted in the inclusion of increased amounts of condensable hydrocarbons in the soot deposit. The greater presence of condensable material promoted decreased deposit thicknesses, larger deposit densities, different deposit morphologies, and higher thermal conductivities.

FUEL 119

Ultilization of solid amine sorbents for the capture of carbon dioxide

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ABSTRACT

Solid amine sorbents were prepared by using a mixture of linear and branched primary, secondary, and tertiary amines. These amines were immobilized within polystyrene (PS), silicon oxide (SO), or polymethylmethacrylate (PMMA) based substrates at various weight ratios. Testing was conducted in various reactor systems where the reactive water required for the capture of carbon dioxide (CO2) was tracked during the adsorption/desorption cycles by mass spectrometer gas analysis. The water management for these sorbents was quantified and used to determine the technical feasibility of the operating conditions for the capture of carbon dioxide from simulated flue gas streams. In addition, the heats of reaction and performance capture capacities of these sorbents were also determined by differential scanning calorimetric (DSC) and thermal gravimetric analyses (TGA) in dry and humid CO2 gas streams. The regenerable solid amine sorbents investigated in this study exhibit acceptable CO2 capture capacities of 2.5 – 3.5 mole CO2/kg sorbent by TGA analysis and within a laboratory-scale reactor. These sorbents were stable over the adsorption/desorption temperature range of 25-100 oC for 10 cyclic tests.

According to the DSC analysis, the reaction energy generated by these sorbents was in the range of 400-600 Btu/lb CO2, which will require a reactor with exceptional heat management capabilities. These thermo-chemical and performance data will be systematically correlated and used for the technical evaluation of sorbent-based, CO2 post-combustion capture systems. A system analysis will also be conducted to identify key parameters that can significantly impact the sorbent reactor design for post-combustion carbon dioxide capture.

FUEL 120

Understanding heterogeneous mercury chemistry

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Density Functional Theory calculations have been performed to predict the binding mechanism of mercury flue gas pollutants such as Hg0, HgCl, and HgCl2 on both organic and inorganic materials. The inorganic materials considered are periodic surfaces of pure Pd (001) and Au (001) and their binary alloys. Inorganic methods for Hg capture are advantageous since they allow for its removal at elevated temperatures, which is applicable for both PCC and IGCC processes. Throughout these sorbent investigations, it has been found that the Pd surface is more reactive than the Au surface to the pollutants of coal combustion flue gas. Calculations for Hg0 binding on PdAu (111) have shown that small additions of Au to Pd increases the binding energy by improving the surface reactivity of the alloy. Organic-based materials have also been considered using both cluster and periodic surface calculations. These organic-based simulations can be applied for increased understanding of heterogeneous Hg activity on simulated soot particles or simulated activated carbon. The elucidation of heterogeneous Hg chemistry will allow for increased understanding of its life cycle throughout the combustion process, by providing a detailed mechanism of its oxidation to its capture. Oxidized mercury is captured by wet scrubbers, while gaseous elemental mercury passes through the scrubbers readily. Particulate matter such as fly ash, unburned carbon and activated carbon can be used to capture elemental and oxidized mercury through adsorption processes. Activated carbon is currently used by many power plants facilities effectively. Understanding the mechanism by which mercury adsorbs on activated carbon is crucial to the design and fabrication of effective capture technologies for mercury.

FUEL 121

Development of a diesel emissions control system based on a lean NOx trap catalyst and a catalyzed particulate filter

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An engine/aftertreatment system for Dodge Ram pickup truck, introduced by Cummins in 2007, achieves the world's lowest 2010 Environmental Protection Agency (EPA) NOx standard a full three years ahead of the requirements. Reduction of NOx emissions in this system has been accomplished using NOx adsorber and ceramic particulate filter technology.

NOx adsorber catalysts had been identified by the EPA during the 2007/2010 rulemaking process as the key candidate for meeting the NOx emissions reduction challenge. However, its practical implementation required substantial breakthroughs in the understanding of its operation and durability. The complexity originated from the inherently non-steady-state, cyclic operation of the NOx adsorber catalyst. Such operation requires a multifunctional catalyst with a variety of redox and acid-base properties, capable of overall optimal operation across all the above processes.

Also, NOx adsorber catalysts are readily poisoned by sulfur from the engine's fuel and lubricant. Its durability is strongly affected by the periodic high-temperature exposure required remove sulfur from the catalyst surface.

Finally, catalyzed particulate filters, also implemented in this system, represent a mature technology, their application downstream of a NOx adsorber catalyst imposed substantial additional scientific challenges. These challenges required development of substantial new knowledge related to the mechanism and kinetic of oxidation of turbostratic carbon in diesel particulate matter.

In response to these challenges, Cummins and Johnson Matthey have conducted major research work, both internally and in collaboration with National Labs and Universities. In this presentation we will share a number of examples from these focused collaborative efforts, with an emphasis on their impact on the research that led to the design and development of the aforementioned catalyst system.

FUEL 122

Formation and thermal decomposition of nitrites and nitrates on BaO/Pt(111) model catalysts

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BaO/Pt(111) model systems have been prepared to understand the role of the interactions between BaO and Pt on the elementary processes in NOx storage reduction (NSR) catalysis. Adsorption and reactions of NO_2 on BaO films deposited on Pt(111) have been studied using temperature programmed desorption (TPD), reflection absorption infrared spectroscopy (RAIRS) and X-ray photoelectron spectroscopy (XPS). NO_2 reacts with a thick BaO film (> 20 MLE) to form nitrite-nitrate ion pairs at 300 K, while only nitrates form at 600 K. Adsorption of NO_2 on a thin BaO film (~ 2-3 MLE) leads to the formation of nitrites with a small amount of nitrates under UHV conditions at 300 K. However, at elevated NO_2 pressures (> $1x10^{-5}$ Torr) thin BaO films are converted into amorphous $Ba(NO_3)_2$ at 300 K. These amorphous $Ba(NO_3)_2$ films transform into crystalline $Ba(NO_3)_2$ particles at 500 K even at sub monolayer BaO coverages.

FUEL 123

Impact of biofuel blending on diesel soot oxidation characteristics: Implications for aftertreatment catalysts

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Control strategies for diesel particulate filters (DPFs) remain one of the most important aspects of aftertreatment research and understanding the soot oxidation mechanism is key to controlling regeneration. Currently, most DPF models contain simple, first order heterogeneous reactions oxidation models with empirically fit parameters. This work improves the understanding of fundamental oxidation kinetics necessary to advance the capabilities of predictive modeling, by leading to better control over regeneration of the device.

This study investigated the effects of blending soybean-derived biodiesel fuel on diesel particulate emissions under conventional combustion from a 1.7L direct injection, common rail diesel engine. Five biofuel blend levels were investigated and compared to conventional certification diesel for the nanostructure, surface

chemistry and major constituents of the soluble organic fraction (SOF) of diesel particulate matter (PM), and the relationship between these properties and the particulate oxidation kinetics.

FUEL 124

Emissions control technology for the 21st century

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Of all of the advances in environmental technology in the past 40 years, few have made as great an impact on society as the 3-way catalytic converter. Intense global research and development activities have resulted in catalysts which can reduce emissions of carbon monoxide, hydrocarbons, and nitrogen oxides by over 90% and which can maintain activity well beyond 100,000 miles of use. Despite this amazing achievement, global environmental regulations and the increasing cost of precious metals continue to drive emissions control scientists and engineers to create more efficient and more durable materials. This presentation summarizes some recent research activities aimed toward the creation of the next generation of emissions control catalyst. These research efforts are focused on several areas including advanced support materials, fundamental investigations of the catalytic properties of small metal clusters, and advanced analysis and characterization techniques.

FUEL 125

First-principles modeling of coverage-dependent rates of catalytic oxidations

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Catalytic reactions of O_2 are ubiquitous in heterogeneous catalysis, and the control of catalytic oxidations has gained even greater prominence in the drive to develop a sustainable energy enterprise. The late transition metals are common oxidation catalysts, and the intrinsic activities of these materials are often observed to depend sensitively on the coverage of surface species, in particular chemisorbed O. The catalytic oxidation of NO to NO_2 over Pt is a prime example

of a catalytic oxidation that can only be described by accounting for the effect of O coverage on the rates of surface reactions. In this work, we use density functional theory (DFT) simulations to characterize the structures, energies, and rates of the key reaction steps in catalytic NO oxidation over Pt(111) as a function of adsorbate coverage. We develop a microkinetic model that properly accounts for observation, and using simple correlations, show how the model can be extended to other metals and to CO oxidation at high oxygen coverage conditions.

FUEL 126

Catalyst by design: Combining the power of theory, experiments, and nanostructural characterization for catalyst development

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We have recently started efforts to develop a “catalyst by design” protocol that iteratively employs theoretical modeling and experimental results to systematically design a catalyst. In this approach, a variety of catalysts are first examined by theory and the most promising candidates are then synthesized experimentally, characterized, and tested.

In our presentation, we report on our “catalyst by design” efforts employing supported platinum clusters. We will describe the nanostructure of Pt clusters and its interactions with CO and NO and compare it with theoretical studies. We will also summarize nanostructural changes in Pt clusters under CO and NO oxidation conditions. Our experiments on model catalysts validate theoretical studies and suggest that “catalyst by design” protocol can be highly effective in catalyst design provided it can be validated for a complex catalyst system such as emission treatment catalyst.

FUEL 127

Interaction of combustion gases with CaO (100) surface: Adsorption kinetics and dynamics

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Catalytic activity of CaO (100) surface towards CO, CO_2, and NO was studied by means of temperature programmed desorption, molecular beam scattering and quantum *ab initio* calculations. NO adsorption leads to formation of dimers, which subsequently dissociate into N_2 and N_2O in TPD. Interaction of CO with CaO (100) surface is relatively weak (E_d = 24 - 45 kJ/mol), while CO_2 forms a number of structures on CaO (100) with higher binding energies (E_d = 30 - 83 kJ/mol). However, initial adsorption probability, S_0, of CO is greater than S_0 of CO_2. MPW3LYP DFT calculations reveal that CO bonds to Ca sites and CO_2 adsorbs only on oxygen surface atoms resulting in formation of carbonates. Both computational and molecular beam scattering results are consistent with the simple mass matching model. CO adsorption obeys direct Langmuirian adsorption dynamics, and CO_2 interaction with CaO (100) surface is precursor-mediated.

FUEL 128

New developments in the science of clathrate hydrates

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We may expect that understanding gas hydrates at the molecular level will help our efforts to learn about natural gas hydrates and to control hydrate processes at all stages. For instance, recognizing that nucleation is almost always heterogeneous under conditions where hydrates are encountered, allows one to focus on inhibiting hydrate nucleation, growth, or both, once one understands the action of the inhibitor. Also, the fact that in many hydrate-forming venues - both laboratory based and natural, nucleation is a localized so that many nucleation events can take place means that the hydrate product may also be quite non-uniform. Often it is assumed that hydrate properties do not depend a lot on the nature of the guest, yet, suitably sized molecules can act either as hydrate guests or inhibitors, suggesting that there may well be a continuum of properties. Here, we present both modeling and experimental results that link macroscopic and guest molecular properties.

FUEL 129

Nucleation and growth of clathrate hydrates studied with a coarse-grained water model.

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There is a need for a kinetic and mechanistic model able to evaluate conditions under which clathrate nucleation and growth can be promoted or inhibited. Understanding of the mechanism of nucleation by atomistic simulations is hampered by the cost of producing the long simulation runs needed to see the rare nucleation events. We use a coarse-grained water model to study clathrate formation. The model is successful in producing the nucleation and growth of clathrates from supercooled water and methane-like molecules, as well as the growth of the guest-free clathrate hydrates of both structure I (sI) and structure II (sII). We find that gas hydrate nucleation occurs through ordering of water around guest molecules. Individual cages do not appear to be stable in the solution; they are subcritical nuclei. Our results suggest that several cages – sustained by the favorable positioning of guest molecules- are needed to reach the critical nucleus size.

FUEL 130

Molecular dynamics simulation of hydrate lattice distortion

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Accurate prediction of the temperatures and pressures where hydrates are stable is important for the development of production strategies using advanced reservoir simulation codes. At present, these codes use algebraic relationships based on existing phase behavior data to determine when hydrates decompose or form. The current state of thermodynamic model development to predict phase behavior clearly demonstrates the need to incorporate a lattice distortion effect. Ideally a thorough description of lattice distortion of hydrates would require an extensive experimental effort; however, the use of molecular dynamics simulation (MDS) is an attractive approach for a systematic study of lattice distortion due to these effects. MDS results are presented on the effects of temperature, pressure, and guest size on lattice distortion. All of these effects were found to be

significant. An important fundamental finding is that appropriately-sized guests can cause a lattice to expand or contract, an observation not previously reported.

FUEL 131

Phase equilibrium and cage occupancy calculations of CO_2 hydrates using an ab initio intermolecular potential

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Gas hydrate reservoirs are receiving increased attention as potential locations for CO_2 sequestration, with CO_2 replacing the methane that is recovered as an energy source. In this scenario it is very important to correctly characterize the cage occupancies of CO_2 to correctly assess the sequestration potential as well as the methane recoverability. A potential energy surface (PES) between H_2O and CO_2 was computed at the MP2/aug-cc-pVTZ level and corrected for BSSE by using half of the counterpoise correction. Intermolecular potentials were obtained by fitting Exponential-6 and Lennard-Jones 6-12 models to the *ab initio* PES, correcting for many-body interactions. The pure CO_2 hydrate equilibrium pressure was predicted with an average absolute deviation of less than 2% from the experimental data. Predictions of the small cage occupancy ranged from 22-38% and the hydration number for the CO_2 hydrate was calculated to be above 7.0, whereas the large cage is fully occupied.

FUEL 132

Investigation of methane hydrate growth using molecular dynamics simulation

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Molecular dynamics simulation is used to investigate steady-state methane hydrate growth in a system larger than 50 sI hydrate unit cells for durations greater than 100ns without employing artificial mass or heat transport constraints. Molecular dynamics simulations are initiated from partially ordered configurations, and as solid hydrate grows it replaces areas of the simulation box previously occupied by a methane and water vapor/liquid system. At the interface of growth, partially formed cages are observed to persist for up to 10 nanoseconds while halo-like hydrogen-bonded networks of water molecules

eventually form the remainder of the cages. The estimated growth rates for these simulations are between 1.3 cm/s and 3.4 cm/s.

FUEL 133

Gas hydrate formation and dissociation using high pressure DSC

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Calorimetry is a more and more used analytical technique to determine compositions, dissociation enthalpies and heat capacities of gas hydrates. As high pressure is needed for such investigations, an innovative methodology (patent of the French Institute of Petroleum) has been developed to produce a High Pressure MicroDSC to be adapted to the determination of thermodynamic properties and kinetics of gas hydrate formation and dissociation.

The High Pressure MicroDSC has a vessel of 0,7 cm3 and operates up to 1000 bars (14 500 psi) in a temperature range from –45°C up to 120°C.

The high pressure DSC technique is especially adapted for the investigation of gas hydrates in various fields;

- flow assuranceapplications

- formation and dissociation of gas hydrates (especially methane for gas hydrate transportation)

- characterization of natural gas hydrates

- plugging of natural gas pipelines

- plugging of annulars (offshore extraction)

- formation of hydrogen hydrates (hydrogen storage)

- formation of CO2 hydrates (CO2 sequestration)

FUEL 134

Activity enhancement of MgO-doped Ag/Al2O3 catalyst for selective catalytic reduction of NOx with methane in the presence of SO2 and H2O

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The performance of selective catalytic reduction of NOx by methane (CH4-SCR) was investigated over MgO-doped Ag/Al2O3 in the presence of SO2 and H2O. MgO addition significantly decreases the active temperature window of NOx conversion. Compared with Ag/Al2O3 catalyst, Ag/MgAl2O4 catalyst exhibits the higher SO2 and H2O tolerance for CH4-SCR at low temperature range of 300□`400°C. For Ag/MgAl2O4, only five percent decrease of NOx conversion happened in the presence of 100ppmSO2 and 15%H2O. The slight decrease in catalytic activity over Ag/MgAl2O4 exposure to SO2 is attributed to the partially deactivation of alumina sites poisoned by SO2. The competitive adsorption between NOx and SO2 in alumina sites is inhibited effectively by MgO addition. The apparent activation energy of CH4-SCR reaction over Ag/MgAl2O4 is equal to 94.6kJ/mol.

FUEL 135

Dual-stage approach for aftertreatment of lean burn natural gas engine exhaust

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A highly active two-stage catalytic system is investigated for the reduction of NO with methane from lean-burning engine exhaust. The first stage is the catalytic oxidation of NO over 10%Co/ZrO_2, aimed at helping NO reduction to proceed with greater selectivity by converting NO to NO_2, which is a more easily reduced species than NO. The second stage is catalytic reduction of NO_2 with hydrocarbons over 0.3%Pd/SZ. Gas chromatography and chemiluminescent NO_X analysis were employed to test the catalysts under simulated lean exhaust conditions. The dual-catalyst system is capable of achieving N_2 yields of above 90% in a broad temperature window of 450-550≡C. The results also show that the dual-catalyst system is very active for the elimination of CO, C_3H_8, C_2H_6 and CH_4. Along with catalytic activity testing under simulated lean exhaust conditions, presented results include temperature-programmed desorption, XPS and DRIFTS. Effect of water vapor on catalytic activity is also investigated.

FUEL 136

Evaluation of a new approach for NOx removal from the flue gas in lab-scale

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A chemical absorption-biological reduction integrated approach is developed to achieve the NO_x removal from the flue gas. In this integrated process, NO (the primary component of NO_x) is chelated by Fe(II)EDTA and subsequently reduced to N_2 by microorganism. Fe(III)EDTA formed via oxidation of Fe(II)EDTA by oxygen in the flue gas is simultaneously and biologically reduced back to Fe(II)EDTA. During the steady state operation, the integrated approach for the NO removal can be achieved to 90%, in comparison with 29% by the water-based biofilter. Moreover, full breakthrough of NO was observed in the scrubbing process after 5 h of operation at the same condition. Two dedicated bacterial strains (a Fe(II)EDTA-NO reducing bacterium and Fe(III)EDTA reducing one) were isolated and characterized. The competition between Fe(III)EDTA and Fe(II)EDTA-NO reduction was also investigated with the mixed cultures.

FUEL 137

Low emissions with microemulsion fuels

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The advantageous effects of water-diesel-emulsions on the combustion have been repeatedly studied over the past thirty years. However, the thermodynamic instability of emulsions has remained an unsolved problem. In a new approach we developed water-fuel-microemulsions, which are thermodynamically stable. We paid special attention to high efficiency and temperature invariance. Furthermore, using biogenic additives, as well as microemulsifying of biogenic fuels such as Biodiesel and BtL (Biomass to Liquid) contributes to environmental sustainability. In a number of combustion investigations on the engine test benches we were able to confirm a reduction of 70% to 80% of soot exhaust concomitant with a substantial NOx reduction during engine operation. Thus, the diesel dilemma or soot-NOx-trade-off is overcome.

FUEL 138

NOx control technologies in a semi-industrial pilot: Experimental study and computational fluid dynamics (CFD) modeling

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An experimental and modeling study of NOx removal technologies by using methane and ammonia as reducing agent has been performed on a semi-industrial pilot with a well known features flue gas. A parametric study has been realized to analyze the main parameters effect on the efficiency of the NOx reduction technologies. By using methane as reducing agent, a high NO removal efficiency up to 90% was observed with the optimal working parameters. With ammonia, 86% of maximum NO reduction was obtained at [NH3]/[NO] = 5.0 and burnt gas temperature of 920°C. The hybrid technique that uses the CH4/NH3/N2 mixtures for NO reduction showed a highly effective approach. A doubled NO removal performance was achieved at 900°C with the injection of small amounts of CH4. Subsequently, a Computational Fluid Dynamics simulation with Fluent code was performed to describe the gas flow in reactor, and the turbulence effects on reducing agents homogeneity.

FUEL 139

Plasma-assisted C3H8-SCR over Co-In/H-beta catalyst for NOx abatement

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A notably enhanced activity in NOx reduction by a two-stage system composed of a non-thermal plasma (NTP) followed by the selective catalytic reduction by C3H8 (C3H8-SCR) over Co-In/H-beta catalyst was observed at a relativity low temperature range from 548 K to 598 K. The optimum active temperature of Co-In/H-beta in complex system was shifted from 648 K to 598 K as compared with C3H8-SCR. In contrast to treatment by the NTP alone, the two-stage system converts mostly NO to nitrogen, without NO2, nitrogen-contains or organic components formed. In the lean oxygen condition, NOx removal is limited; during the excess oxygen, considerable NO and C3H8 was oxidized to NO2 and nitrogen-contains in NTP stage, then transformed to N2 over Co-In/H-beta catalyst.

FUEL 140

Ultrahigh capacity coprecipitated manganese oxide sorbents for oxidative mercury capture

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Novel manganese oxide-based sorbents prepared by co-precipitation with a support have been prepared for mercury (Hg) removal from gas streams. Under the laboratory test conditions used, exceedingly high breakthrough capacities of up to ca, 15 % w/w Hg have been achieved using zirconia as the support compared to approximately 2.0% for neat precipitated manganese oxides and ca. 0.1% w/w for an activated carbon (AC) which has widely been used in direct injection trials for flue gases from pulverised fuel (PF) combustion. According to the expected mechanism, Hg(0) is oxidised to Hg(II), the captured form. Variable temperature measurements and temperature programmed desorption have indicated that the capacity remains high until above ca. 1500°C, confirming that strong chemical, as opposed to physical, adsorption occurs. Further, SO2 does not impair the performance of the sorbents until temperatures above 150oC.

FUEL 141

Aromatic production from biomass by catalytic fast pyrolysis

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Aromatics can be produced from cellulosic biomass by catalytic fast pyrolysis. This process first involves pyrolysis of the solid biomass to smaller oxygenates. These smaller oxygenates then enter into the zeolite pores and undergo a series of decarbonylation, decarboxylation and oligomerazation reactions to produce aromatics, CO, CO2 and water. The reaction is shape selective and both the shape of the zeolite and the active site are critical in this reaction. We have tested a range of catalysts and reaction conditions to optimize aromatic production. Experiments have been performed in batch reactors, fixed bed reactors and a fluidized bed reactor. Isotopic studies have helped us identify the reaction mechanism and the key reaction intermediates. This appears to be a

very promising process to economically produce petrochemicals from renwable biomass resources.

FUEL 142

Catalytic cellulose conversion in ionic liquids

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Among various biomass feed sources, cellulosic sources are favored because of their abundance in nature and the fact that they do not fall in the food chain for animals or humans. One promising platform chemical derived from cellulosic biomass is 5-hydroxymethylfurfural (HMF) that is suitable for polymer synthesis or liquid biofuels. For the first time, we present a unique “single-step” catalytic process that depolymerizes cellulose rapidly under mild conditions and converts to HMF. The catalytic transition metal chlorides were dissolved in imidazolium based ionic liquid (1-ethyl-3-methylimidazolium chloride) at temperatures of 80-120°C to perform cellulose depolymerization and the subsequent production of HMF with high selectivity. In parallel with bio-enzymatic method, our discovery shows a promising route for transforming abundant renewable biomass cellulosic resources into a liquid fuel suitable for the transportation sector, and help to diminish our reliance on petroleum.

FUEL 143

Designing reforming catalysts for conditioning biomass derived syngas for liquid fuel synthesis

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The efficient thermochemical conversion of biomass to produce liquid fuels using indirect gasification requires the use of a catalytic steam reforming process to

remove and reform tars to produce clean syngas which additionally maximizes the use of the biomass carbon and hydrogen content. The catalysts used in the steam reforming reactor can comprise a significant portion of the overall process cost to produce biofuels. In order to reduce the catalyst cost and improve the overall fuel synthesis economics, highly active and stable catalysts are required. To achieve this goal, we are using rational catalyst design to understand, design, and synthesize robust, tailor-made catalysts capable of handling biomass-derived impurities such as tars, polyaromatic hydrocarbons (PAHs), H2S, and other trace contaminants such as HCl and various alkali species. Results of this work will be discussed.

FUEL 144

Kinetics of a coupling catalytic reaction for producing biodiesel using high acid value oils

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Kinetics of an esterification-hydrolysis coupling reaction for producing fatty acid methyl esters (biodiesel) using high acid value waste restaurant oils were studied in laboratory and pilot plant reactor systems, sulfuric acid and surfactant being used as catalysts. The one-step process for producing biodiesel was carried out in micellar catalysis using a surfactant. The mode of adding methanol was mainly investigated. The experimental results indicat that stepwise addition of methanol shortens reaction time to 4.5 hours in the conversion of 96%. Based on experimental data, kinetics of the esterification-hydrolysis coupling reaction was set up.The kinetic parameter E and A for hydrolysis reaction are 80 kJ/mol and $3.7x10^{10}$, for esterification reaction are 50 kJ/mol and $1.4x10^{10}$, respectively. The results calculated from the kinetic equations are in accordance with the experimental results. An optimal reaction condition was given for high biodiesel yield and a reaction mechanisum was proposed. The performance of biodiesel from waste restaurant oils is determined using standard methods.

FUEL 145

High density hydrocarbon fuels from renewable feedstocks

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High density, fully saturated mixtures of multicyclic hydrocarbon dimers derived from beta-pinene have been synthesized by dimerization with the heterogeneous catalysts montmorillonite K10 (MMT-K10), Nafion, and Amberlyst-15. MMT-K10 and Nafion proved to be efficient dimerization catalysts, while Amberlyst-15 was sluggish and produced only isomers. By controlling the reaction temperature, yields of up to 83% dimer have been achieved with no detectable trimer. As determined by GC/MS and NMR spectroscopy, the primary reaction pathway is through isomerization of beta-pinene to camphene followed by dimerization to a complex mixture. Other important products include the strained cyclic molecule tricyclene and the dehydrogenated isomer p-cymene, both of which limit the overall yield of dimer. Hydrogenation over PtO_2 at ambient temperature yielded a fully saturated product with a density of 0.932 g/mL. This value approaches that of JP-10 (0.94 g/mL) suggesting that these new mixtures may have uses as tactical fuels.

FUEL 146

Catalytic gasification of automotive shredder residues with hydrogen generation

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Catalytic gasification of automotive shredder residues (ASR) for the generation of high-purity of hydrogen and then integrated to a fuel processor is economically and environmentally attractive. Thus, the objective of the present work is to investigate a ASR catalytic gasification for generating hydrogen using 15 wt.% NiO/Al2O3 catalysts. In a lab-scale fixed-bed downdraft experimental approach, catalytic gasification of ASR has accompanied by a substantial production of syngas at 760-900 K. Most of the Ni(II) reduced to Ni(0) is confirmed by the XANES spectra. The EXAFS data also show that the central Ni atoms have a Ni-O and a Ni-Ni with bond distances of 2.03 ± 0.05 Å and 2.46 ± 0.05 Å, respectively. In addition to over 87% of syngas generation, approximately 3.42 ×105 kcal h-1 of thermal energy is recovered and cold gas efficiency is 76-85% when the gasifier was operated at O/C atomic ratios between 1.1 and 1.3.

FUEL 147

Considerations for catalyst properties required for S-I thermochemical cycle applications

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One promising route for hydrogen production involves the splitting of water by thermochemical sulfur-based cycles that employs the catalytic decomposition of sulfuric acid into SO2 and O2. We have arrived at the following criteria for catalyst selection: Potential catalysts will probably need d or f electrons. Though having d electrons, supported noble metals catalysts will not work because of sintering effects. Materials must be stable under the extreme oxidizing conditions of a H2SO4 environment at 850 °C. Therefore, they should probably be oxides. In addition, they should be transition metal, or rare earth, oxides that do not sinter, sublime or disproportionate (e.g., with melting points above about 2300 °C). Because of the harsh, oxidizing environment, constituent metals should be in the highest oxidation state. Oxides should not form undesirable compounds such as very stable sulfates. Finally, oxides should be reasonably economical, and should not present major environmental issues.

FUEL 148

Theoretical study of ammonia-borane dehydrogenation pathways: Homogeneous catalysis and aminoborane oligomerization

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The chemistry of ammonia-borane dehydrogenation is theoretically studied from the perspectives of homogeneous catalysis and thermolysis. A variety of interesting mechanisms and intermediates that are difficult to observe experimentally are elucidated, including the nature of the active catalyst in the Ni NHC system and the importance of NH2BH2 in understanding aminoborane oligomer formation. The role of free carbenes in the Ni NHC system is also hypothesized.

FUEL 149

Neutron- and Raman-scattering measurements of hydrogen dynamics in clathrates hydrates

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Hydrogen clathrate hydrates have raised strong interest recently as possible materials for hydrogen storage. In these compounds, H_2 molecules are hosted in “cages” formed in the hydrogen-bonded H_2O lattice. They represent a paradigmatic example to study the quantum dynamics of confined hydrogen molecules. In this talk the results of recent inelastic neutron scattering and Raman spectroscopy measurements will be presented and discussed. The measurements have been performed on heavy water clathrates containing molecular hydrogen or HD, with completely deuterated tetra-hydrofuran (THF). In the high-resolution neutron spectrum the H_2 (or HD) molecule excitations give rise to very strong bands, which are assigned unambiguously to rotational transitions of the H_2 molecule, to center-of-mass translational transitions (rattling) and to combinations of these. The Raman spectra reveal details of the interaction of the H_2 molecule with the cage, and of the different number of molecule in the cages.

FUEL 150

Quantum dynamics of small clusters of hydrogen molecules inside nanocages of clathrate hydrates

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Clathrate hydrates with hydrogen molecules as guests have emerged recently as potential hydrogen storage materials. The dynamics of molecular hydrogen inside the clathrate nanocages is highly quantum mechanical. We will present the results of rigorous quantum five-dimensional calculations of the translation-rotation levels of one H_2, D_2, and HD molecule inside the small cage of the sII clathrate hydrate, on two intermolecular potential energy surfaces. Direct comparison will be made with the recent inelastic neutron scattering and Raman

spectroscopy experiments. We will also discuss diffusion Monte Carlo (DMC) calculations of the size evolution of the energetics and the vibrationally averaged spatial distributions of small clusters with up to five H_2 and D_2 molecules in the large cage of the sII clathrate hydrate. The DMC results regarding the maximum occupancy of four H_2 and D_2 and their geometry within the cage are in excellent agreement with experiment.

FUEL 151

Thermodynamic stability of hydrogen clathrate hydrates

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The cage occupancy of hydrogen clathrate hydrate has been examined by grandcanonical Monte Carlo simulations for wide ranges of temperature and pressure. The simulations are carried out with a fixed number of water molecules and a fixed chemical potential of the guest species so that hydrogen molecules can be created or annihilated in the clathrate. It is found that the smaller cage in structure II is practically incapable of accommodating more than a single guest molecule even at pressures as high as 500 MPa. The larger cage is found to encapsulate at most 4 hydrogen molecules but its occupancy is dependent significantly on the pressure of hydrogen. We also examine the cage occupancies of some mixed hydrates containing both hydrogen and polar molecules, the latter of which serve to reduce the pressure to be applied.

FUEL 152

Gas hydrates and semiclathrate hydrates for H_2 and CH_4 storage: Kinetics, capacity and stability

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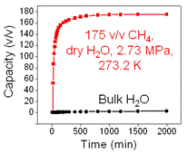
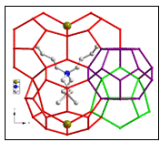
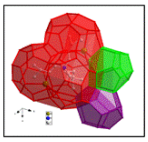
Gas hydrates (or clathrates) have potential advantages as materials for hydrogen or methane storage with respect to other gas storage technologies. For example, hydrates can trap gases such as hydrogen close to ambient temperature, quite unlike porous materials where cryogenic temperatures are required. We show that substantial quantities of methane (around 45 v/v) can be stored reversibly in certain semi-clathrate hydrate structures at atmospheric pressure and ambient

temperature, again in contrast to physisorption approaches. Several challenges exist: for example, the quantity of hydrogen stored in gas hydrates is well below the Department of Energy (DoE) target of 6 wt. %. By contrast, pure methane hydrate in "dry water" form stores 175 v/v gas: that is, very close to the corresponding DoE target. This presentation will discuss approaches to storing gases (H2 and CH4) in hydrated form, in particular strategies for accelerating hydrate formation kinetics, minimizing storage pressure (ideally to 1 atm), and maximising gas storage capacity.



FUEL 153

Studies of clathrate hybrid compounds

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Hydrogen storage from two independent sources of the same material represents a novel approach to the hydrogen storage problem, yielding storage capacities greater than either of the individual constituents. Here we report a novel hydrogen storage scheme in which recoverable hydrogen is stored molecularly within clathrate cavities as well as chemically in the clathrate host material. X-ray diffraction and Raman spectroscopic measurements confirm the formation of â-hydroquinone (â-HQ) clathrate with molecular hydrogen. Subsequent to clathrate decomposition, the host HQ was used to directly power a PEM fuel cell. With one H2 molecule per cavity, 0.61 wt% hydrogen may be stored in the â-HQ clathrate cavities. When this amount is combined with complete dehydrogenation of the host hydroxyl hydrogens, the maximum hydrogen storage capacity increases nearly 300% to 2.43 wt%. Adaptation of this storage scheme to other higher energy content host molecules may provide a route towards feasible high energy content storage materials.

FUEL 154

Hydrogen storage in clathrate materials

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Significant challenges remain for suitable hydrogen storage materials capable of storing sufficient quantities of hydrogen for practical purposes. Clathrate hydrates are one class of materials partially suitable for the storage of hydrogen; however, the maximum storage capacity in clathrate hydrates is presently insufficient to meet the critical storage limits. The pressure and temperature conditions for hydrogen storage have reached manageable limits in sII hydrates. Type-VI hydrates present another potential storage material, and are reported to undergo a structural transformation to sII when pressurized with methane gas, which is the first constraint for storage applications using such materials. In this study, we report our experimental results on the tert-butylamine hydrate system. Preliminary studies indicate that the structural transformation to sII occurs even when pressurized at 258 K. Our results on XRD and Raman spectroscopy will be discussed to provide insight into the gas storage and structural changes in this material.

FUEL 155

In situ elevated temperature electron microscopy of catalysts with single-atom resolution using a novel MEMS-based heater technology

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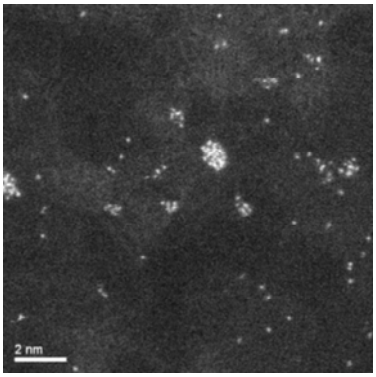
With the advent of aberration-corrected electron microscopes that provide sub-Ångström image resolution, it is of great interest to study the behavior of catalytic materials at elevated temperatures while maintaining the resolution capabilities of the microscope. In collaboration with Protochips Inc., our laboratory is developing a new paradigm for in-situ heating stage technologies. A MEMS-based heater chip having a ceramic membrane 0.5mm square both supports the catalyst sample, and heats the sample by current passed through the membrane. The small mass, rapid heating (~106 °C/s), and symmetry of the device provide highly stable operation that permits imaging mononuclear catalytic species. Example applications (e.g. Au/Fe2O3 and Ir/MgO) will be presented.



FUEL 156

Bimetallic PdZn catalysts for the steam reforming of methanol

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ZnO-supported palladium-based catalysts have been shown in recent years to be both active and selective towards the steam reforming of methanol, although they are still considered to be less active than traditional copper-based catalysts. In this work, we prepared $Pd/ZnO/Al_2O_3$ catalysts which were exposed to in-situ oxidation reduction cycles, and were characterized by XRD, TEM, EDS, and FTIR in order to elucidate their bulk and surface characteristics. We show that our Pd-based catalysts are not only more active than Cu-based catalysts after the initial 48 hour deactivation period, but they can be easily regenerated by oxidation in air at 420ºC followed by re-exposure to reaction conditions at 250ºC. Reduction at high temperatures (>420ºC) led to Zn loss from the alloy nanoparticle surface resulting in lowered catalyst activity. However, the catalysts exhibited self-healing properties as activity was regained with time on stream under reaction conditions alone. These findings illustrate that the nanoparticle surface is dynamic and changes drastically depending on the environment leading to highly stable catalysts, and that elevated reduction temperatures are not necessary to achieve high CO_2 selectivity as commonly believed for PdZn alloy catalysts.

FUEL 157

Atomic scale imaging of platinum based catalysts for polymer electrolyte membrane fuel cell cathodes

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Aberration-corrected scanning transmission electron microscopy (STEM) is being used to characterize the sub–Å–scale atomic structure of Pt–based electrocatalysts, which are used in the cathodes of polymer electrolyte membrane (PEM) fuel cells. Structural characteristics of the catalysts nanoparticles that are of particular interest include the surface structure (as related to composition, atomic ordering, and particle faceting), surface area (as related to particle size, dispersion, and overall particle morphology), and relationship of individual particles with the carbon support material (i.e., bonding). The contributions of each of these catalyst structural parameters will ultimately determine the activity (for the oxygen reduction reaction) and long-term stability of a particular catalyst in the cathode. In addition to initial characterization of as-prepared catalysts, in-situ, high–resolution microscopy techniques are being used to evaluate the stability of potential cathode catalysts under relevant PEM fuel cell exposures and to identify the mechanisms of catalyst degradation. These studies utilize specially designed holders for the aberration–corrected STEM to expose fuel cell catalysts to temperature, water-vapor, and potential cycling and track changes to individual catalyst particles. The behavior of several catalyst compositions during in-situ microscopy exposures will be discussed.

FUEL 158

Patterns of reactivity for alcohols on cerium oxide thin films

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Ceria catalysts are commonly used in many fuel related processes such as the Water-gas-shift reaction, alcohol reforming, and fuel cell applications. Alcohol adsorption and reaction, in particular the branching between aldehyde and alkene formation in longer chain alcohols, has been identified as a method for understanding acid/base and redox properties of metal oxide catalysts. We have studied the adsorption of ethanol and propanol on well-ordered CeO_2(111) thin films in order to understand the reactivity associated with specific adsorption sites, the influence of O-vacancies and the importance of oxide reducibility. 2-propanol produces propylene almost exclusively whereas primary alcohols (ethanol and 1-propanol) produce significant amounts of aldehydes. O-vacancies

promote alkene formation. 2-propanol acts as an oxidant on reduced ceria but has little effect oxidized ceria. The primary alcohols act as reductants. Exposure of ceria to all of the alcohols at elevated temperatures leads to total decomposition to CO and H_2 and ceria reduction.

FUEL 159

XANES Studies of sulfur poisoning in Rh, Ni catalysts for steam reforming of liquid hydrocarbons

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Three catalysts, CeO_2 modified Al_2O_3 supported monometallic 10%Ni, 2%Rh, and bimetallic 2%Rh10%Ni catalysts were tested for steam reforming reaction of Norpar13 (ExxonMobil) at 800 ^oC with the presence of 350 ppm organic sulfur. X-ray absorption near edge spectroscopy (XANES) was successfully applied to the sulfur poisoned catalysts, and identified a few sulfur species including sulfides, adsorbed sulfur poison, sulfonate and sulfate. The significance of the current findings is two-fold: 1) the existence of the other sulfur species besides sulfides manifests that the long-believed sulfur poisoning mechanism, the formation of metal sulfides, needs to be reconsidered; 2) the presence of sulfate and other sulfur species indicates complicated involvements of sulfur in the hydrocarbon chemistry. Thus, the current results suggest that the deactivation effects of other sulfur species besides sulfides and the influence of sulfur on the other deactivation processes such as carbon deposition should be included in the sulfur poisoning mechanism.

FUEL 160

Essential role of surface hydroxyls for the stabilization and catalytic activity of TiO2-supported gold nanoparticles

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We report the investigation of titania supported gold catalysts prepared by magnetron sputtering. Catalysts grown on natural fumed titania were structurally unstable resulting in the rapid coarsening of 2.3 nm gold clusters into large ~20 nm gold clusters in a few days at room temperature under normal atmospheric conditions. However, treating the titania support powder to a mock-deposition-precipitation process, at pH 4 or pH 10, followed by the subsequent deposition of gold onto this treated powder produced a remarkable enhancement in gold particle stability and a 20-40 fold enhancement of catalytic activity respectively. This enhancement can not be attributed to the formation of oxygen vacancies on the TiO2 surface. Instead, it appears to be associated with the formation of strongly bound hydroxyl species on the TiO2 surface. The formation of surface hydroxyls during the deposition-precipitation method is coincidental and contributes significantly to the properties of Au/TiO2 catalysts.

FUEL 161

Structure of Au-nanoparticles on oxide supports: X-ray scattering and PDF study

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The catalytically active sites are on or near tiny catalyst particles that are difficult to structurally characterize, and the catalyst-coated or dispersed surface is usually very heterogeneous and thus structurally ill-defined. Standard diffraction techniques are of limited use because catalytic nano-sized particles are highly dispersed and/or structurally disordered. In this study we used the atomic pair distribution function (PDF) analysis to characterize nanocrystalline gold particles on the oxide substrate. We have examined atomic structure of the gold nanoparticles deposited on several oxide supports. These included 4% wt. Au on TiO2/SiO2, TiO2/Al2O3 and SiO2. Using resonant x-ray scattering at the Au L absorption edge we resolved PDF peak that may represent special bonding between gold nanparticles and the substrate. We also performed high energy x-ray scattering to study, in situ, evolution of the structure with temperature. These studies revealed substantial particle coarsening above 400 ºC.

FUEL 162

CO2 reduction and formation of organic molecules on pyrite surface and pyrite surface supported cubane clusters

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Pyrite formation is postulated to be coupled to the catalytic formation of small inorganic molecules that eventually lead to the emergence of large organic molecules necessary for the formation of life. It is recently demonstrated that a large range of small inorganic molecules can be formed in the presence of FeS/NiS species. To understand the mechanisms of CO2 reduction we carried out extensive calculations of the CO2 reduction on pyrite surfaces, clusters of FeS species, and cubane like structures that form on the pyrite surfaces. Our calculations show that the reduction of CO2 to carbonyl boned to metal centers is energetically favorable. We also compare the formation and reactivity of pyrite surface supported cubane structures with the cubane structures that naturally occur in CO2 reduction enzymes. Our exploration of Fe-S cubane structures can potentially lead to efficient CO2 reduction catalysts that mimic or exceed the activity of biological counterparts.

FUEL 163

Coal contributions to the overhead liquids obtained from co-coking in a laboratory scale delayed coker

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ABSTRACT

Coking and co-coking of decant oil and decant oil/coal blends were studied using a large laboratory-scale delayed coker. Four different coals were used in this study: Powelton/Eagle, Canterberry, Pittsburgh, and Marfork. Two petroleum-based decant oils were used for delayed coking and co-coking purposes. In the co-coking experiments, the coal was reacted at 20 and 30% by weight in the

blend. Coker pressure was adjusted to two different values for evaluation. Co-coking of decant oil/coal blends produced higher amounts of coke than coking of decant oil alone. Product distribution ranges for co-coking were found to be 22-39% coke, 50-71% liquid, and 1-16% gas. Increasing the amount of coal in the blend and coker back-pressure resulted in a higher percentage of coke formation (which resulted in coke of lower quality), while the total liquid product yield decreased. The objective of this study was to determine molecular contributions from coal to the overhead liquid. The isolated overhead liquid products were subsequently vacuum-distilled into typical refinery boiling range materials (gasoline, jet fuel, diesel and fuel oil). Vacuum distillates were further characterized using GC/MS to investigate the effect of particular coals on the liquid produced from co-coking. GC/MS analyses demonstrated that vacuum fractions of co-coking overhead liquid had higher quantity aromatic components than those of coking. On the other hand, vacuum distillation results showed that co-coking of coal with a decant oil at a higher coal percentage (30 wt% versus 20 wt%) in the blend increased the lighter boiling range materials (i.e., gasoline, jet fuel, diesel) in the overhead liquid. In addition, it was found that higher coker back-pressure (50 psig versus 25 psig) also increased the lighter boiling range materials in the overhead liquid.

FUEL 164

Understanding carbon dioxide adsorption on coal

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An attractive option for sequestration of CO2 is injection into unmineable coal seams and organic-rich shales. Combined, these sources represent more than 10% of technically recoverable natural gas in the U.S. Methane strongly adsorbs to coal surfaces but is displaced when CO2 is injected. Gas shales may similarly desorb methane with the adsorption of CO2, making them another potential option for CO2 sequestration while enhancing methane recovery. A major obstacle in CO2 sequestration by coal and gas shale is insufficient understanding of the molecular-scale processes involving CO2 sorption on organic matter at pressures and temperatures of interest. Within this work, experimental approaches coupled to computational modeling on relevant organic samples are investigated to determine surface properties and structure, sorption, and transport mechanisms within these systems, with the ultimate goal of identifying optimal locations for methane recovery and simultaneously, long-term CO2 sequestration.

FUEL 165

Directly capturing aromatic structural features in coal via "Fringe3-D" generating 3-D molecular models directly from HRTEM lattice fringe images

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Advances in image processing allow the extraction and analysis of digital lattice fringe images from high-resolution transmission electron microscopy (HRTEM) micrographs. They have previously been used to determine coals aromatic structural distribution for fringe length, interlayer spacing, structural alignment, and the number of layers per stack. The HRTEM lattice fringe images of coals were used, for the first time, to directly generate a 3D coal molecular "slice" representation of the aromatic moieties utilizing "Finge3D" in-house software. The lattice fringes are characterized by length, shape or curvature, and orientation. These are effectively captured and re-generated to produce 3D coal molecular "slice" consisting of the aromatic structural contribution in 3D space with very limited depth. The approach presented here will be useful in reducing the effort required to generate coal and other carbon-rich, molecular models (e.g. coals/chars, soot, carbon black, activated carbon, etc), at scale, with more realistic structural feature distribution.

FUEL 166

Survival of aliphatic biomarkers in high rank coals

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At relatively low maturities, kerogen-bound aliphatic biomarkers released via hydropyrolysis invariably display retarded thermal maturities compared to their "free" counterparts due to the protection afforded by the macromolecular structure. This study investigates the release hopanes and steranes at high maturities from a rank series of UK bituminous coals to follow their alteration at the stage where concentrastions of surviving aliphatci carbon is extremely low. Remarkably, the bound biomarkers survive in anthracite with a relatively small degree of alteration compared to their lower rank counterparts. In most cases,

ring isomerisation within the kerogen-bound phase is still more retarded. For a corresponding series of artificially matured coals via hydrous pyrolysis, both “free” and “bound” phase side chain maturation are significantly retarded.

FUEL 167

Direct liquefaction of selected Chinese and American coals

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Three coal samples rich in barkinite, and two others, rich in semi-fusinite, from China and America, respectively, were selected for liquefaction in tubing bomb microreactors. The samples were pulverized to –100 mesh and dispersed in tetralin; hydrogen pressure was 1000 psig (cold). Composition was determined by maceral analysis. Two of the barkinite-rich samples were found to be extremely high in volatile matter, hydrogen content, and H/C atomic ratio. The high conversion and the yield of oil and gas were related to the high barkinite content, H/C atomic ratio and pyrite content. The opposite effect was observed from the high semi-fusinite samples. Liquefaction of the third barkinite-rich coal under a variety of conditions indicated that the values of yield of oil and gas and conversion were related to the heating procedure. The yield of preasphaltenes and asphaltenes seemed not to be extremely effected by the amount of catalyst added or by changes in heating procedures.

FUEL 168

Relationship between relaxation of hydrogen bond by solvent polarity and the extraction yield of hypercoal

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Ashless coal (HyperCoal; HPC) was produced by thermal extraction at 360 oC using a mixed solvent of 1-methylnaphthalene (1-MN) and indole (IN). The extraction yield increased with increasing the concentration of IN. The rate of increase in the extraction yields varied with the coal rank, depending on the content of oxygen. Under 13% of oxygen in raw coals, the rate increased with oxygen. This trend may be related to the weight composition of different oxygen functional groups.

FUEL 169

Does water pressure retard coalification?

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This study investigates the effect of water phase and liquid water pressure on coalification and associated hydrocarbon generation. Using a vessel and a pressure of up to 500 bar, a U.K. bituminous coal (Lomngannet) and a Tertiary coal (Svalbard, Norway) were pyrolysed under nonhydrous, hydrous at steam pressure (<160 bar), and high water pressure (500 bar) conditions at 350oC for 24 hours. The vitrinite reflectance and Rock Eval pyrolysis results, and products yield clearly indicate that maturation and hydrocarbon generation were both retarded by water pressure. Bitumen and liquid hydrocarbon generation were enhanced under hydrous conditions when compared to nonhydrous conditions, while at high water pressure the yield of bitumen was reduced but liquid hydrocarbon generation was not significantly affected. Gas generation was also significantly reduced at 500 bar water pressure compared with experiments performed under nonhydrous and normal hydrous conditions.

FUEL 170

Effect of oxide catalysts and oxygen-conducting supports on partial oxidation of liquid hydrocarbons

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Reforming liquid hydrocarbons into H2 and CO rich gas streams for solid oxide fuel cells requires a catalyst system with thermal stability and resistance to deactivation in the presence of contaminants. Many of the liquid fuels considered appropriate for this application contain sulfur and aromatic compounds that can poison and deactivate metal-based catalysts, specifically through carbon formation. A series of supported Ni and Ni-substituted oxides were compared for activity and carbon resistance for the partial oxidation (POX) of n-tetradecane (TD) in the presence of added dibenzothiophene and 1-methyl naphthalene. Bulk Ni-substituted barium hexaaluminate (BNHA) catalysts were compared to systems with BNHA layered over an oxygen-conducting support (OCS) or a higher surface area alumina support. The supported materials demonstrated marked improvement in performance over the pure metal and bulk BNHA catalysts. Temperature programmed oxidation of the catalyst beds after the runs revealed a significant reduction in carbon formation when the OCS was used. The stability provided by substituting Ni into hexaaluminate layers limits the clustering of active Ni sites, which has been suggested to limit deactivation caused by a concerted sulfur poisoning reaction. Additionally, when BNHA is supported on an OCS, the oxidation of deposited coke precursors is promoted by the transfer of gas phase oxygen to the active sites, reducing carbon formation in the bed. The catalysts were also characterized by BET, ICP, XRD, and H2 Pulse-chemisorption dispersion analysis

FUEL 171

Catalysis of electrochemical and partial oxidation of CH_4

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The direct electrochemical oxidation of hydrocarbons in the SOFC (solid oxide fuel cell) could offer significant advantages: (i) elimination of a complicated reformer unit, (ii) the production of a nearly pure CO2 exhaust stream for the direct CO2 sequestration and (iii) low investment and maintenance cost due to the simplicity of the process. The extreme operational temperature of a SOFC at 700-1000 °C provides a thermodynamically favorable pathway to deposit carbon on the most commonly used Ni anode from CH4 according to the following reaction (CH4 = C + 2H2), thus deteriorating the cell performance, stability and durability. Development of an effective catalyst for the CH4 SOFC requires a

fundamental understanding of the mechanism of the electrochemical oxidation of CH4 on the anode catalyst surface. This presentation will report results of an experimental study of the electrochemical oxidation of CH4 on a Cu-Ni-cermet anode, focusing on (i) the microstructure and performance characteristics (current-voltage performance) of Ni and Cu-Ni anode before and after a long term exposure of CH4, (ii) mechanistic study of direct CH4 partial oxidation reaction on Ni and Cu-Ni anode catalyst. The examination of the microstructure by SEM and EDAX of the Cu-Ni anode after exposure to CH4 suggested that addition of Cu to Ni-cermet induced a significant carbon tolerance to the SOFC. The results of XRD and Impedance spectroscopy results for H2 and CH4 fuel will be discussed.

FUEL 172

Feasibility of using sulfur as a growth promoter for CNx PEM and DMFC ORR catalysts

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PEM and direct methanol fuel cells (DMFCs) have great promise as clean and efficient mobile energy conversion devices. Before the widespread commercialization of these fuel cells can be realized, significant material cost reductions must occur. The greatest material costs in PEM and DMFCs are associated with the platinum cathode catalysts. Nitrogen containing carbon nanostructured (CNx) catalysts have been studied as a replacement to the platinum cathode catalysts in both PEM and DMFCs. These CNx materials are produced by acetonitrile pyrolyis at high temperatures over nanofiber growth catalysts. To increase the yield of the CNx grown, sulfur, in the form of thiophene, has been investigated as a fiber growth promoter. The impact of the use of sulfur on the resulting CNx catalyst has been examined using both catalyst characterization and electrochemical techniques.

FUEL 173

Effect of pretreatment on Pt-Co cathode catalysts for the oxygen reduction reaction

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The use of highly dispersed platinum crystallites on high surface area carbon increases the active surface area and electrocatalytic activity of the electrocatalysts, thereby reducing the Pt loadings in the cell. About four times the loading of the anode is currently used at the cathode to help account for the low activity of the Pt electrocatalyst for the oxygen reduction reaction (ORR). Although improvement in catalytic activity by alloying Pt with transition metals has lead to lower loadings in the cathode, loadings are still one order of magnitude higher than the DOE target for 2015. In order to reduce the precious metal loading without sacrificing activity and stability, a new method for the preparation of bimetallic catalysts is proposed.

FUEL 174

Binary and tertiary platinum based alloys as anode surface catalysts for direct methanol fuel cells

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Platinum fcc alloys are the core of prevalent direct methanol fuel cell (DMFC) anode catalyst. During methanol oxidation CO is strongly adsorbed on the catalyst surface reducing of the number of Pt sites required for the oxidative adsorption of methanol. Adsorbed CO poisons the Pt surface, thus pure Pt is considered to be a poor catalyst for efficient DMFC operation. Binary alloys of Pt with oxophilic metals (Ru,Os) have been investigated in the past to serve as DMFC anode catalysts of improved electrocatalytic activity with respect to pure Pt. Periodic Density Functional Theory (DFT) calculations on carbon monoxide (CO) adsorbed atop over PtRu, PtOs binary alloys and PtRuOs tertiary alloy surfaces are used to elucidate the weakening of the C-O and C-Pt bonds upon alloying Pt with Os and Ru atoms as manifested by C-O, C-Pt stretching frequency (ν_{CO}, ν_{CPt}) reductions and CO_{ads} adsorption energy reduction. Mulliken population analysis, density-of states spectra and electron density contour maps analysis of the CO orbitals (from 4σ to 2π^*) and their apparent interactions with the metal lattice bands are used to examine the validity of a modified σ-repulsion π-attraction scheme. Analysis of the apparent electron density transfers from the metal towards the CO and *vice versa* and the spatial distribution of the CO-Pt hybridized molecular orbitals reveals that the C-O bond weakening is predominantly due to π-bonding reduction accompanied by σ-bonding enhancement whereas C-Pt weakening is attributed to spatial redistribution of the CO electron density and its accumulation towards the oxygen atom region thus reducing the C-Pt π-bond. Concomitantly systematic increase of electrostatic repulsion as of σ CO orbitals and sp-Pt both increase their electron densities upon alloying Pt with Ru, Os atoms further weaken the C-Pt bond.

FUEL 175

Pt/Carbon electrocatalysts functionalized with phenylsulfonic acid and perfluorooctylphenyl groups

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Pt/carbon electrocatalysts that have been functionalized via diazonium-based chemistry with phenylsulfonic acid and perfluorooctylphenyl groups show a variety of interesting properties, and these electrocatalysts can help us understand the impact of catalyst support surface properties on electrode performance and durability. For example, we have found that the presence of phenylsulfonic acid groups on the surface of Pt/Vulcan improves the electrode proton conductivity, but the electrode will then tend to flood even at low ionomer content (I/C = 0.4). The presence of hydrophobic perfluorooctylphenyl groups on the surface of Pt/Vulcan results in behavior similar to unmodified Pt/graphitized-Vulcan. Preliminary results indicate that at least some of these effects are due to changes in ink properties that influence the microstructure of the catalyst layer in the MEA.

FUEL 176

Mechanism of the thermal decomposition of furan

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Furan (C_4H_4O) is one of many important products in biomass pyrolysis. To understand the thermal cracking of furan, we have studied its thermal decomposition by entraining a few Torr in 1–2 atmospheres in a high temperature supersonic nozzle. Furan samples are heated to temperatures of 1000 – 1400 K for 30–50 μsec. The decomposition products are identified by photoionization mass spectroscopy and infrared spectroscopy.

When we decompose furan in a hyperthermal nozzle the reaction products are identified by features in the PIMS at m/z 40 and 42. In separate experiments,

infrared signatures of $HCCCH_3$, CO, HCCH, and CH_2CO have been detected when the reaction products are trapped in a cryogenic matrix. As the nozzle temperature is raised to 1400 K, the PIMS spectrum shows peaks at m/z 39 (the propargyl radical, $HCCCH_2$) and m/z 41 (ketenyl radical, HCCO, or allyl radical, CH_2CHCH_2).

FUEL 177

Thermal decomposition of anisole and the methoxyphenols

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A major component of biomass is lignin, a complex molecule found in plant cell walls. Lignin contains cross-linked aromatic rings with methoxy and hydroxy groups. When lignin is pyrolyzed, anisole (methoxybenzene), the methoxyphenols and their derivatives are liberated and undergo further decomposition. With the use of a hyperthermal pulsled nozzle and photo-ionization mass spectrometer, we have studied the thermal decomposition of anisole, methyl-deuterated anisole, fully deuterated anisole and 2, 3 and 4-methoxyphenol. Our results show consistent, predictable fragmentation patterns. In anisole, the first fragmentation step is the loss of methyl radical from the methoxy group to form phenoxy radical. Phenoxy radical then loses a CO to form cyclopentadienyl radical. Analogous fragmentation is observed in the methoxyphenols in the presence of a hydroxy group. In our anisole pyrolysis experiments we observe a bimolecular reaction resulting in the formation of methylcyclopentadiene and detect fulvene or benzene from its subsequent decay.

FUEL 178

Thermal degradation pathways of levoglucosan as an intermediate in cellulose pyrolysis

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Levoglucosan (1,6-anhydro-a-D-glucopyranose) is an important intermediates in cellulosic biomass pyrolysis since it is the major anhydromonosaccharide formed during cellulose pyrolysis. We have studied thermal decomposition pathways of levoglucosan using photoionization time-of-flight mass spectrometry (PI-TOF-MS) equipped with hyperthermal nozzle. The pyrolysis oven temperature was varied in range of 190-1300 °C. As a complimentary study, pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) analysis was used to identify pyrolysis products at 300-700 °C. Comprehensive thermal decomposition reaction mechanisms were proposed based on the pyrolysis products of levoglucosan identified. High-level energy calculations using the CBS methods were employed to verify proposed reaction mechanisms in the levoglucosan pyrolysis.

FUEL 179

Pyrolysis reactions of lignin-rich corn stover residue in a laminar entrained flow reactor

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Thermochemical conversion of biomass yields a complex slate of light gases, condensable vapors and refractory aromatic tars. However, the detailed reactions and the kinetic parameters that govern their formation are not well known. To address this problem we have designed a laminar entrained flow reactor (LEFR) to pyrolyze solid biomass samples from (300-950 °C) with detection by molecular beam mass spectrometry (MBMS). The variation in spectra over the temperature range was analyzed using multivariate curve resolution with optimization by alternating least squares (MCR-ALS). Spectral data from the flow reactor obtained at small increments of temperature over a wide range allows for finer resolution of the changing product slate, and hence the details of the underlying reaction mechanism.

FUEL 180

Formation of liquid products from solid fuel in filtration combustion

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The objectives of this investigation were: 1) to measure the yield and composition of liquid gàsification products for different fuels in the regime of filtration combustion; 2) to preliminary assess the prospects of different fuels and processing regimes to recover liquid components with simultaneous power generation; 3) to develop an efficient yet simple enough system to recover liquid products formed in the course of gasification.

The experiments were carried out in a 46-mm inner diameter laboratory reactor made of fused quartz. In order to reduce the heat loss, the side walls of the reactor were screened with aluminum foil. During the experiments, the temperature profiles were registered and gaseous products were sampled. Air gasification of various solid fuels was investigated.

Cellulose, wood, peat, brown coal, and rubber were gasified in the regime of filtration combustion. Humidity of the fuels was within 10%. Air was used as an oxidizer. Aerosol of liquid products was separated from gas stream by enhancing turbulence of gas. To estimate the quality of liquid products separation, the gas stream was passed through two consequent water-cooled condenses.

The recovery of liquid products was about 90%. Humidity of those products was 25-30%.

The element analysis of the liquid products showed that carbon and hydrogen content in them not less and in certain cases was significantly higher than those in the raw fuel. In processing of the fuels with high ash, the content of the mineral fraction in the tar formed was much lower.

FUEL 181

Global mechanisms of tar formation during biomass gasification

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Biomass gasification is a promising method for converting raw biomass into syngas, which can then be conditioned into various types of transportation fuels. One benefit of gasification is that it is thought to be insensitive to feedstock. In

order to take advantage of this feedstock flexibility, it is necessary to understand the effects of feed material upon process efficiency. In particular, it is important to understand the formation of unwanted products such as tars. These unwanted products need to be removed from the syngas, and existing clean up technologies add significant cost to the process. An understanding of byproduct formation as a function of feedstock composition will help facilitate the development of cost effective syngas cleanup methods. In order to investigate tar formation, different materials were gasified in a pilot gasification facility. A Molecular Beam Mass Spectrometer (MBMS) was used to measure the hot gas composition and comprehensive correlations of the products were analyzed using Interactive Self-modeling Multivariate Analysis (ISMA). This helped to identify the global chemistry of the system and trends of tar formation and composition are identified.

FUEL 182

Rate estimation rules for H abstraction reactions from alcohols by H atoms and CH3 radicals

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The thermal conversion of biomass to syngas, bio oil or other high-value products is severely hampered by the lack of a fundamental understanding of the elementary reaction steps that take place. Given that two of the three major components of biomass (cellulose and hemicellulose) contain several OH groups per polymer unit, we suspect that H abstraction reactions from the OH group or from adjacent C-H bonds play a significant role. Therefore we used electronic structure calculations at the CBS-QB3 level combined with transition state theory to calculate H abstraction rate constants for a set of alcohols. We considered H atoms and CH3 radicals as abstracting reactants, because the concentrations of both species are probably higher than those of other reactive radicals. The obtained individual rate constants for a given reaction class are then generalized to rate estimation rules. These rate rules can then be applied to larger molecules for which high-level calculations are not possible.

FUEL 183

Rate constants for the elimination of water from alcohols and biomass model compounds

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Various cellulose decomposition schemes consider dehydration of cellulose or its primary pyrolysis products as an important reaction step in the process. One possible dehydration reaction is the direct water elimination in the gas phase. To test the feasibility of this reaction class, we performed electronic structure calculations at the CBS-QB3 level combined with transition state theory to calculate high-pressure rate constants of this reaction class. The results for a set of nine alcohols showed that the rate constants follow similar patterns that allow us to generalize them in terms of rate estimation rules. We also used the reaction set to investigate the performance of two lower-level methods, B3LYP/6-31G(d) and CBS-4M levels, because the CBS-QB3 method cannot be used for more realistic biomass model compounds such as cellobiose. Although the B3LYP rate constants appear to agree well with the CBS-QB3 results, further investigations provide evidence that this is a fortuitous coincidence and that the B3LYP results are in fact not reliable. The CBS-4M results are in general more precise than B3LYP but the barriers differ by 2-3 kcal/mol from the CBS-QB3 data. Finally we expanded the investigations to OH containing multifunctional molecules such as hydroxyl aldehydes, cyclic hemiacetals and others. Comparison to simple alcohols shows that some adjacent functional groups clearly increase the H2O elimination rate constant. Overall, however, the calculated rate constants are too small to have a significant impact on the pyrolysis chemistry of biomass, except perhaps at the highest temperatures (i.e., T> 1000K).

FUEL 184

Self-assembly synthesis and functionalization of mesoporous carbon materials for catalysis and energy applications

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Porous carbon materials are ubiquitous in catalysis, separation, and energy storage/conversion. Well-defined nanoporous carbon materials are essential for a number of the aforementioned applications. Ordered mesoporous carbon materials have previously been replicated using colloidal crystals and presynthesized mesoporous silicas as scaffolds. Recently, we have reported alternative methods for the synthesis of highly ordered mesoporous carbons via self-assembly. The mesostructures of these carbon materials are highly stable and can be further tailored via graphitization and surface functionalization for catalysis applications. This presentation will be focused on our recent development in (a) new self-assembly approaches to the preparation of highly ordered mesoporous carbon materials for controlling pore structures and

morphologies and (b) surface modification techniques to control the interfacial chemistry of nanoporous carbon materials for catalysis applications.

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FUEL 185

Influence of devolatilization residence time on the reactivity of modified drop-tube furnace coal chars

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For pulverized fuel combustion unburnt carbon is now causing considerable issues, presenting the opportunity to develop an effective coal combustion catalyst and thereby obviate the need for post-treatment of pulverized fuel ash. Therefore, coal chars containing possible catalyst candidates were generated on the medium scale using a drop-tube furnace (DTF) and on the small scale using a thermogravimetric analyzer (TGA). It was subsequently concluded that chars produced on the TGA are more reactive than those from the DTF. Residence time was also confirmed as being an important factor during devolatilization. Furthermore, whilst all of the compounds investigated increased the rate of coal combustion on the small scale, one exemplary catalyst became deactivated during DTF devolatilization, indicating that TGA studies might form an unsuitable platform for comparing coal combustion catalysts. Nevertheless other catalysts seem to maintain consistent behavior on the TGA and DTF and, for these specimens, mixing of the coal and catalyst prior to devolatilization appears favorable.

FUEL 186

Hydrogen spillover: Its "diffusion" from catalysis to hydrogen storage community

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Dissociative adsorption of hydrogen on catalyst sites followed by surface diffusion (spillover) to a carbon support was first reported for Pt-carbon catalysts (Robell, 1964) and was soon accepted as a valid step of numerous catalytic reactions. However, the concept of metal-assisted hydrogen storage (Schwarz, 1988) based on spillover entered much later the hydrogen community (Lueking and Yang, 2002) and is gaining recognition slowly as an alternate approach for enhancing hydrogen storage capacity of microporous materials for fuel-cell powered vehicles. This talk will analyze the significance and limits of the spillover mechanism for adsorptive storage of hydrogen, with examples of enhanced hydrogen uptake on Pd-containing activated carbon fibers. Evidence of the atomic nature of spilt-over hydrogen will be presented based on experimental results from inelastic neutron spectroscopy studies. Research sponsored by the Division of Materials Sciences and Engineering, U.S. Department of Energy under contract with UT-Battelle, LLC.

FUEL 187

Activity and structural characterization of activated carbon-supported catalysts for diethyl carbonate synthesis

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The synthesis of diethyl carbonate (DEC) by gas-phase oxidative carbonylation of ethanol can be achieved using a $CuCl_2$-$PdCl_2$/activated carbon catalyst (CPAC). However, DEC activity decreases with time on stream. In addition, the nature of Cu and Pd species before and during catalysis is unclear. CPAC activity towards DEC was explored by variation of metal loadings, He pretreatment, and addition of alkali promoters. Several techniques – x-ray diffraction, x-ray absorption spectroscopy (Cu, Pd, Cl), and scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS) – were used to complement activity measurements and provide insights into the structure of CPAC catalysts (i) as prepared; (ii) after pretreatment in He; (iii) under reaction conditions. Cupric chloride was partially reduced to Cu(I) species in the fresh catalyst, and full reduction to Cu(I) took place upon exposure to He or reaction gases. Cl loss was observed. $[CuCl_2]^-$ and $PdCl_2$ were proposed as the active species.

FUEL 188

Advances in wire mesh reactor and diagnostics

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In an effort to further understand the coal gasification behavior in entrained-flow gasifiers, a high pressure and high temperature wire mesh reactor with new features was recently built. An advanced LabVIEW-based temperature measurement and control system was adapted. Gaseous species from wire mesh reactor were quantified using a high sensitivity gas chromatography. The material balance of coal pyrolysis in wire mesh reactor was demonstrated for the first time by improving the volatiles quantification techniques.

FUEL 189

CFD modeling of gas phase tar chemistry in a fluidized-bed biomass gasifier

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A limitation of biomass gasification in a fluidized-bed reactor is the high level of tars in the product gas, causing fouling and hazardous waste. A possible approach would be to directly optimize the gasifier design and operating conditions to the biomass properties for minimal tar production. However, it requires a better understanding of the detailed chemical and physical processes occurring simultaneously in the reactor. CFD offers a unique opportunity to incorporate fundamental results, for example from detailed chemical modeling, into a larger scale framework, allowing to gain some global insight on tar reduction methods. In this work, a detailed chemical mechanism is assembled, that accounts for biomass devolatilization, decomposition of primary products, and formation of aromatic rings and PAH. The chemical model is then integrated into CFD simulations of turbulent fluidized-bed reactors to study the effect of mixing processes and inhomogeneity on the amount and composition of tar at the exit of the gasifier.

FUEL 190

Development of fundamentals-based gasification kinetic model

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GE Global Research is conducting an international R&D program on gasification kinetics. The goal of the program is to develop and validate predictive models describing the chemical processes in the gasification and post-gasification zones of practical gasification systems. This paper describes ongoing activities in this program that aim at development and validation of a fundamentals-based gasification kinetic model.

Separate sub-models are used to describe each of these process steps. The overall gasification process is re-constructed by integration of the sub-models into an integrated model. Each sub-model development generally follows the following scheme:

1. Assessment of state-of-the-art and downselection of the best available sub-model;

2. Identification of knowledge and data gaps;

3. Sub-model improvement and coding;

4. Sub-model validation and adjustment based on available bench- and pilot-scale experimental data;

5. Submodel reduction and integration;

6. Validation of the integrated model.

The validated submodels are integrated in a detailed gasification kinetic model that will be used as a kinetic tool for optimizing the processes in gasification systems. The detailed kinetic model will be then reduced using special mechanism reduction procedures and will become a basis for a new computational fluid dynamics (CFD) model. The resulting CFD tool will also be used for improving current and future gasification system designs.

FUEL 191

Kinetics of catalytic steam gasification of HyperCoal

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HyperCoal is a clean coal with ash content <500 ppm. Pasir [PAS] (C= 68 %) coal was subjected to solvent extraction method to prepare Pasir HyperCoal [PasHPC]. Kinetics of K_2CO_3 catalyzed steam gasification of Pasir HyperCoal was investigated at 600, 650 and 700 °C. Catalyst was loaded by physical mixing approach as HyperCoals do not mix with water. Effect of catalyst loading on gasification rate was studied at 6, 10, 20, 40, and 50 % catalyst loadings. Gasification rates were strongly influenced by the temperature and catalyst loading. Catalytic steam gasification of HyperCoal was chemical reaction controlled in the 600~700 °C temperature range with an activation energy around 125 kJ/kmol.

FUEL 192

Prediction of Chinese coal ash fusion temperatures in an H2 atmosphere

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The ash fusion temperatures of twenty-one typical Chinese coal ash samples and sixty synthetic ash samples were measured in a H2 atmosphere. The computer software package FactSage was used to calculate the liquidus temperature and predict phase equilibria of synthetic ash samples. Empirical liquidus models were derived to relate the AFTs of sixty synthetic ash samples with their liquidus temperature calculated by FactSage. The liquidus model were used to predict the AFTs of twenty-one Chinese coal ash samples in a H2 atmosphere and then the ash behavior in a H2 atmospheres was analyzed. The results show that in a H2 atmosphere, there was an apparent linear correlation and good agreement between the AFTs of synthetic ash samples and the liquidus temperatures calculated by FactSage. These liquidus models predict the AFTs of coal ash samples with a good level of accuracy. Some of the iron oxides in coal ash samples fused under a H2 atmosphere were reduced to metallic iron.

FUEL 193

Prediction of thermal decomposition of biomass using reaction MD

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Reactive molecular dynamics was used to explore the thermal decomposition of several biomass model compounds. We used ReaxFF methodology developed by the Goddard group at Cal Tech [van Duin et al. 2001; Strachan et al., 2005; Chenoweth et al., 2008]. It is a general bond-order-dependent potential in which van der Waals and Coulomb forces are included from the beginning. The parameters are obtained from QM calculations and the most recent version is parameterized for CHNO systems, as is necessary to explore biomass reactions. Calculations have been carried out for compounds representative of cellulose (glyceraldehyde, β-D-glucopyanose, β-cellobiose, cellulose I), hemi-cellulose (β-D-xylofuranose, D-mannopyanose), and lignin (methoxybenzene, ethoxybenzene, phenethyl phenyl ether.) In all cases the predicted primary products are those observed experimentally or suspected from bond strength and or transition state analysis.

FUEL 194

Pressurized spent pulping liquor gasification kinetics

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Spent liquors are biomass residues from the kraft pulping process. They contain dissolved lignin and hemicellulose together with inorganic pulping chemicals. The high alkali metal content in the liquors (~ 20%) and the molecular dispersion of the alkali metal with the carbon matrix make the gasification rate an order of magnitude faster than for most biomass fuels. The aim of this research was to obtain pressurized black liquor gasification rate data at conditions relevant for pressurized entrained flow gasifier: temperatures of 900-1000°C, high heating rates, and char that has been produced simultaneously with gasification.

The kinetics was evaluated in a pressurized entrained flow reactor. The isothermal conditions and constant reactant gas concentrations allow for extraction of kinetic constants. Pyrolysis and gasification experiments were made in the pressure range of 5-20 bar, temperature of 900°C, and varying gas concentrations (CO_2, H_2O, H_2, CO).

The char carbon yield after devolatilization (initial pyrolysis) was independent of pressure. For the liquor studied here, approximately 60% of liquor carbon was present as fixed (organic carbon) after devolatilization, 20% had formed carbonate, and 20% had volatilized. The fixed carbon gasification rate depended on the partial pressures of CO_2, H_2O, CO, and H_2. At 5 bar, 80-92% of the fixed carbon that remained after devolatilization became gasified between 1 and 4 seconds. At 20 bar, 0-33% of the fixed carbon became gasified in the same time interval. With high CO and H_2 contents, there was very little gasification at 20 bar.

Of previously published black liquor gasification rate models, a best fit to the rate data was obtained by H_2O gasification model which included a forward rate by H_2O only and inhibiting effects of CO and H_2. An improved fit was obtained with a generalized Langmuir-Hinshelwood type model, which also included an inhibiting effect by CO_2.

FUEL 195

The importance of char structure in determining high temperature, high pressure gasification rates

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High temperature rate measurements were made for reaction with CO2 of chars produced from two Australian coals using a high pressure entrained flow reactor. Low temperature (intrinsic) rate measurements were made on the same chars using an atmospheric pressure fixed bed reactor and a high pressure thermogravimetric apparatus.

The measurements clearly show the impact of pore diffusion limitations on high temperature gasification rates and reflect the impact of the different morphologies of the char samples. Gas adsorption and optical image analysis methods were used to differentiate the relevant structural features of the char particles to enable the effects of pore diffusion and chemical reaction processes to be deconvoluted. By characterising and considering the sample as a mixture of significantly different physical structures (thin-walled cenospheres, spongy porous particles, solid porous particles) the intrinsic reactivity data could be successfully reconciled with the high temperature gasification rate measurements.

FUEL 196

The role of a Langmuir-Hinshelwood formulation in understanding high pressure char gasification kinetics

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This paper summarises results and analyses of recent investigations into the kinetics of coal char gasification reactions at high pressures in mixtures of reactant and product gases. The data are used to demonstrate the applicability of the Langmuir-Hinshelwood formulation, and also to highlight some important aspects of the formulation that may complicate its use more generally for high pressure gasification reaction systems.

Reaction rate data are presented for reaction of two Australian coal chars with CO2 and steam at pressures up to 2MPa. The work has highlighted two important phenomena: the competitive inhibition between CO2 and H2O for active surface on a reacting char particle; and the impact of CO partial pressure on the reaction rate.

By accounting for the impact of CO2 adsorption on the surface site concentration available to H2O, the LH kinetic scheme is able to describe well the overall kinetics in mixtures of H2O and CO2.