

SYMPOSIUM HH
Advanced Catalytic Materials - 2000

November 29 – 30, 2000

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* Invited paper

8:30 AM *HH1.1

CROSS-LINKED LIQUID CRYSTAL ASSEMBLIES AS CATALYTIC ORGANIC ANALOGS TO MOLECULAR SIEVES. Douglas Gin, Seth Miller, Esther Kim, David Gray, Mary Reppy, Wenjing Zhou, Scott Hammond, Univ of California at Berkeley, Dept of Chemistry, Berkeley, CA.

A new class of organic, nanoporous heterogeneous catalyst is described. Cross-linked, nanostructured polymer networks based on a carboxylate-containing amphiphilic liquid crystal exhibit enhanced basicity and can catalyze the Knoevenagel condensation. These materials maintain their ordered structure in solvent and can be recycled. In addition to enhanced basicity, excellent site accessibility, substrate size exclusion, pore size control, and processibility prior to cross-linking are features of this nanostructured system. Preliminary results on the incorporation of other reactive groups (e.g., acidic) in these nanoporous materials will also be presented.

9:00 AM HH1.2

ORGANIC-INORGANIC HYBRID MATERIALS VIA ONE-STEP SYNTHESIS. DESIGN OF NEW CATALYTIC MATERIALS. Duncan J. Macquarrie, Dominic B. Jackson, Andrea Watson, Kate A. Utting, Stephane Tailland, James E.G. Mdoe, Dept of Chemistry, Univ of York, Heslington, York, UNITED KINGDOM.

The preparation of highly thermally and solvolytically stable organic-inorganic hybrids has recently been achieved using neutral amine templates. This allows the preparation of a range of materials for different catalytic applications with tunable loading and pore characteristics. The template can be easily recovered and reused, leading to a very atom-efficient synthesis of the material. Recently we have concentrated on the role of preparation conditions on the nature of the materials, in particular the effects of the solvent compositions used for synthesis and solvent extraction. For example, the composition of the solvent mixture (ethanol / water) used for the sol-gel synthesis is broadly similar to that found in all-silica analogues, but with some very significant differences. For example, in aminopropyl containing materials, slight changes of solvent composition can reduce the nucleophilicity of the amine groups dramatically, with little effect on the basicity of the materials. These anomalous materials make excellent catalysts for the Knoevenagel reaction, since grafted aminopropyl materials are deactivated by side-reactions in which the amine behaves as a nucleophile. The catalytic implications of these phenomena, and the importance of textural porosity will be discussed.

9:45 AM *HH1.3

MESOPOROUS METALS FROM LIQUID CRYSTALLINE PHASES: SYNTHESIS AND CATALYTIC PROPERTIES. George Attard, Stephane Leclerc, Stephanie Maniguet, Andrea Russell, Univ of Southampton, Dept of Chemistry, Southampton, UNITED KINGDOM.

Mesoporous oxides, particularly metallosilicates, have attracted considerable interest for potential applications in catalysis because of their combination of uniformly sized pores (2-15 nm diameters) and ultra-high surface areas. Recently we reported that mesoporous metals and alloys can be prepared by chemical or electrochemical routes from precursor mixtures that are in a lyotropic liquid crystalline phase. These metals have unique nano-architectures that are in effect the casts of the structures of the liquid crystalline phases used in the synthesis. For example, platinum prepared by the reduction of hexachloroplatinic acid dissolved in the hexagonal phase of a non-ionic surfactant contains cylindrical pores 2.5 nm in diameter, of indefinite length and disposed on a long-ranged hexagonal lattice. The uniformity of the mesoporous nano-architecture results in materials having very high specific surface areas and exceptional pore connectivity. A particularly interesting consequence of this type of nano-architecture is that the internal surfaces of the metals are concave and with very small radii of curvature (i.e. high curvatures). This surface topology is quite distinct from that encountered in nanoparticulate metals, in which the surface is convex, and suggests that the nature and distribution of surface defects, steps and crystal surfaces in the mesoporous metals may be unusual. We have begun to investigate the catalytic properties of these mesoporous metals, particularly platinum, palladium and platinum/ruthenium alloys in the context of carbon monoxide oxidation, methanol oxidation and hydrogenation reactions. Our results suggest that mesoporous metals do indeed exhibit catalytic properties that are intrinsically different from those of nanoparticulate metals.

10:15 AM *HH1.4

MACROPOROUS MATERIALS PREPARED BY COLLOIDAL CRYSTALLINE TEMPLATING. Andreas Stein, Hongwei Yan, Christopher F. Blanford, Rick C. Schroden, Brian J. Melde, University of Minnesota, Dept. of Chemistry, Minneapolis, MN.

The method of colloidal crystal templating has been applied to a wide range of periodic, macroporous solids, including metal oxides, metals, alloys, zeolites, and hybrid organic/inorganic solids. These materials are prepared by filling the interstices within arrays of uniformly sized, close-packed spheres with a fluid precursor that is subsequently converted to a solid skeleton. Macropores of a few hundred nanometer diameter are obtained after removal of the templating spheres. The product structures (periodicity, void sizes, window sizes, grain sizes in the wall, crystallinity of the wall, porosity of the wall) depend on the type of templating spheres used, methods of ordering them, filling processes, and the thermal/chemical history of the samples. We will discuss the effects of preparation parameters on the product structures, and the implications of the structural features of these materials on catalytic, optical, magnetic, sensing, and electrochemical applications.

10:45 AM HH1.5

USING GRAPHITE NANOFIBERS AS A STRUCTURE TEMPLATE. C.L. Marotta, K.E. Atkinson, R.U. Kirss, R.T.K. Baker, Northeastern Univ, Dept of Chemistry, Boston, MA.

Since the discovery of buckminsterfullerene and nanotubes, graphite nanostructures have been used in a wide variety of applications such as composites, catalyst supports, fuel cell electrodes, and hydrogen storage materials. Graphite Nanofibers (GNF), which are synthesized from the catalytic decomposition of carbon containing gases over metal powders, offer a surface composition that is unique among graphite materials. Traditional nanotube surfaces provide a high basal plane to edge ratio, since they are essentially graphite sheets in a cylindrical formation. Conversely, GNF structures possess a high edge to basal plane ratio, consisting of the zig-zag and armchair configurations. These edge sites interact strongly with materials deposited on their surfaces, and are ideal candidates for a supported catalyst system. In this study, aluminum oxide was deposited onto a platelet GNF template. Alumina supports offer excellent thermal and chemical stability and allow for high dispersion of metal crystallites. Metal particles deposited on GNF edge sites have been found to exhibit strong interactions in these regions, which result in excellent catalytic activity and selectivity when compared to traditional supports. One might expect that a material with the chemical properties of alumina, and the structural characteristics of GNF would offer a set of unique properties. Chemical vapor deposition (CVD), due to its excellent filling capability and conformational specificity, offers the possibility of accomplishing this. The thin film oxides have been characterized by a combination of electron microscopy, thermogravimetric analysis, energy dispersive X-ray elemental analysis, and selected area electron diffraction. Preliminary results show the formation of highly structured films of aluminum oxides, with some retention of the GNF platelet morphology.

11:00 AM *HH1.6

THEORY AND APPLICATIONS OF CERAMIC FOAM CATALYSTS. Martyn V. Twigg, Johnson Matthey, Catalytic Systems Div, Royston, Herts, UNITED KINGDOM; James T. Richardson, Dept of Chemical Engr, Univ of Houston, Houston, TX.

Reticulated ceramic foams can now be prepared from a range of materials, and they have characteristics that makes them desirable as substrates for structured solid heterogeneous catalysts. They can exhibit extremely high porosities with a significant degree of interconnectivity that results in low pressure-drop properties, and high convection in the turbulent megapores results in excellent mass and heat transfer coefficients. Furthermore, ceramic foams, unlike their honeycomb monolithic counterparts with unconnected parallel channels, have a considerable degree of radial transport, which is an advantage in processes limited by heat transfer. The low porosity of ceramic foam means it has to be coated with a higher surface area support material, and this increases pressure-drop and decreases heat and mass transfer coefficients in a predictable way. Reactions requiring short contact times to control product selectivity and processes that are limited in some way by heat removal from within the catalyst structure can benefit from the use of foam-based catalysts. This is particularly true if the efficiency factor for a particular reaction with conventional solid catalyst is low, and a model is developed that incorporates these concepts. Examples of reactions of this type include many industrially important processes, such as the partial oxidation of hydrocarbons, selective oxidation of ammonia to nitric oxide, water gas shift, methanol synthesis, methanation and Fischer Tropsch synthesis. These concepts will be demonstrated with results from some current research that will be augmented with additional data from published papers and patents.

11:30 AM *HH1.7

CARS AS AIR CLEANERS WITH NOVEL METAL SUBSTRATES. Dr. Frank Witzel, Wolfgang Maus, Rolf Bruck, Emitec Inc, Auburn Hills, MI.

During the past decades, car use has increased dramatically. In 1950 there were approximately 27 vehicles per 1000 people worldwide; this ratio rose by a factor of 5-6 to become around 150 vehicles per 1000 people today. Higher mobilization lead to a more prosperous economy in industrial countries and this prosperity, in turn, lead to an even greater increase in mobilization. The USA is a good example of this correlation between mobilization and prosperity: here there are 800 vehicles per 1000 people. In the past two decades, the automobile industry – together with suppliers – has done much to satisfy the need for mobility in an environmentally friendly manner: Catalytic converters were introduced in the late 70's thanks to the preliminary research work of both the car manufacturers and the suppliers. With the continuous improvement in catalyst technology came the expectations for greater emission reductions from the initial 80% to 90-95% today. In 2003, California will introduce SULEV (Super Ultra Low Emission Vehicle) limits. The exhaust systems must be capable to convert more than 99% of the pollution selectively to nitrogen, carbon dioxide and water. Drivers with vehicles meeting SULEV will actually be able to clean the air while being on the road. To meet SULEV limits, the catalytic converter must reach its operation temperature as quickly as possible. To accomplish this, the catalyst must be moved closer to the engine; in other words, from the underfloor position up to the exhaust manifold and sometimes even into the exhaust manifold. In the past, ceramic was used almost exclusively for the underfloor position. However, for the close-coupled position just described, metal became the preferred material. Metal guarantees a quick temperature increase and can withstand the higher stress loads of the catalyst located close to the engine. The use of metal also provides more freedom in designing novel catalyst types and designing new surface structures for higher conversions.

SESSION HH2: NANOCRYSTALLINE CATALYSTS

Chairs: Andreas Stein and Gene S. Smotkin
Wednesday Afternoon, November 29, 2000
Room 201 (Hynes)

1:30 PM *HH2.1

NANOSTRUCTURE PROCESSING OF CATALYTIC MATERIALS. Jackie Y. Ying, MIT, Cambridge, MA.

Nanostructured materials are of interest for a variety of applications. They may be generated by various physical and chemical approaches with ultrahigh surface areas. For example, we have developed hydrolysis-precipitation and hydrothermal synthesis routes to derive nanocrystalline titania-based materials at low temperatures. These materials exhibit size-dependent photocatalytic properties for the effective decomposition of chlorinated compounds at room temperatures. Through reverse microemulsion-mediated sol-gel processing, we have achieved complex oxide nanoparticles with ultrahigh thermal stability. These materials provide for the stable dispersion of transition metal and rare earth oxides, providing for excellent activity in the methane catalytic combustion over a wide range of temperatures. These examples illustrate the uniqueness of nanocrystalline processing, enabling us to design and tailor microstructure, component dispersion, surface reactivity and quantum confinement effects in catalytic systems.

2:00 PM *HH2.2

TITANIA DOPED SILICA NANO-STRUCTURED POWDERS PRODUCED BY THE AERO-SOL-GEL (ASG) PROCESS FOR CATALYSIS OF EPOXIDATION REACTIONS. G. Beaucage, J. Chen, D.J. Kohls, G. Skillas, Department of Materials Science and Engineering, University of Cincinnati, Cincinnati, OH.

The Aero-Sol-Gel (ASG) process is a solvent free synthesis at room temperature that can potentially be used to easily produce, in a continuous process, significant quantities of nano-structured, mixed-oxide powders for catalysis. In this presentation use of ASG mixed-oxides as epoxidation catalysts in simple liquid state reactions of olefins such as octene will be discussed. ASG nano-powders may represent an important new approach to synthesis of heterogeneous catalysts that can be easily produced and chemically and structurally tuned in a solvent free process with limited dependence on miscibility and compatibility of reactants. The ASG process takes advantage of the rapid transport and kinetics of continuous aerosol processes. The epoxidation catalysts discussed here follow ground work in similar catalytic systems produced by solution route sol-gel reactions that was conducted by Davis at the University of Virginia, Baiker at ETH in Zurich and by Neumann at Hebrew University in Jerusalem. These seminal efforts give credence to the idea of using amorphous mixed

oxides as an alternative to crystalline zeolites and supported oxides as epoxidation catalysts. Amorphous mixed oxides may offer a wider range of tunability in terms of morphology and interfacial chemistries when compared to crystalline systems. Additionally, ASG synthesis offers, by far, the least expensive and simplest production route for such catalysts yet proposed.

This work is partially funded by the National Science Foundation (CTS-9986656) and is in informal collaboration with workers at Procter & Gamble, Equistar Chemicals and Goodyear Tire and Rubber.

2:15 PM HH2.3

THE ROLE OF NANOSIZE AND AMORPHOUS Mo IN DEHYDRATION OF CYCLOHEXANE INTO BENZOL. R.T. Malkhasyan, S.L. Grigoryan, Scientific-Production Enterprise Atom, Ministry of Industry and Trade, REPUBLIC OF ARMENIA; T.A. Gharibyan, L.A. Vartikyan, V.T. Minasyan, R.R. Grigoryan, Institute of Chemical Physics, NAS, REPUBLIC OF ARMENIA.

Nanostructured materials are largely used in catalysis processes recently. These materials are obtained by different physical and chemical technologies. In this paper it is introduced the nanostructured amorphous molybdenum Mo (QC), obtained by reducing molybdenum oxide by quantum-chemical technology in hydrogen plasma under room temperature. In order to form a catalyst with developed surface, Mo is applied over γ -Al₂O₃, with specific surface area equal to 60 m²/g and pore radius of 370 Å. It was applied by two technologies: 1a. Mechanical application of Mo (QC) in hexane on γ -Al₂O₃ (after preliminary heat treatment under the temperature of 450°C). 1b. Mechanical application with ultrasonication during 15 min. 2. By saturation of γ -Al₂O₃ of ammonium molybdate, with further drying and reduction: a) with molecular hydrogen, b) quantum-chemical technology. We compared the catalytic activities (CA) of Mo, obtained by the technologies mentioned above, and Mo - crystalline (pure for analysis) in the reaction of dehydration of C₆H₁₂ into C₆H₆, the gas-carrier is H₂, under atmospheric pressure, under T=525°C. It was shown that nanocrystalline and amorphous Mo have high CA in the process of dehydration of cyclohexane. The application of Mo on the surface and pores of the carrier as well results in increase of CA and sometimes cracking. Based on the nanosize and amorphous Mo and W, obtained by QC technology, Mo₂C and W₂C are synthesized under 500-620°C accordingly, having high CA. Thus, the quantum-chemical technology of obtaining catalysts is a perspective technology, from the point of obtainment of higher dispersion active metals and systems based on them (MeC, MeN etc.).

2:30 PM HH2.4

CATALYTIC COMBUSTION WITH NANOCRYSTALLINE PEROVSKITE SYSTEMS. Neeraj Sangar, Jackie Y. Ying, Massachusetts Institute of Technology, Dept. of Chemical Engineering, Cambridge, MA.

Catalytic combustion of methane has been widely studied as an alternative to gas-phase homogeneous combustion. It allows combustion to occur at high levels of excess air, leading to more complete reaction and reduced hydrocarbon emissions. Furthermore, it enables combustion to proceed at lower temperatures, significantly reducing NO_x production. Traditionally, noble metal systems, such as palladium, have been used as combustion catalysts. However, palladium-based catalysts tend to deactivate at the high temperatures of >700°C by phase transition to Pd metal and by sintering. Our research objective is to develop complex perovskite catalysts with high catalytic activity for methane oxidation and good thermal resistance for use as low-temperature ignition catalysts for catalytically-stabilized thermal combustors. To achieve this, we have synthesized nanocrystalline perovskites (La_{1-x}A_xBO₃, A = Sr, Ca, Ba and B = Ni, Fe, Co, Mn) with grain sizes <20nm and high surface areas (~30m²/g) using chemical coprecipitation. The synthesis conditions have been carefully controlled to ensure nanostructured morphology, correct stoichiometry, compositional and phase homogeneity. The catalytic activity of nanocrystalline perovskites for methane combustion has been investigated for different A and B site substitutions in the crystal structure. These novel catalysts allowed for 10% conversion of a stream of 1% CH₄ in air (60,000 h⁻¹) at around 350°C, which is comparable to palladium-based catalysts, with full conversion at around 550°C. The trends in catalytic activity with different A and B site dopants have been explained by investigating the defect chemistry of these perovskites under reaction conditions. Temperature-programmed desorption and coulometric titration of oxygen have been performed to measure the oxygen vacancy concentration in the perovskite structure and the nature of the surface oxygen species, which is responsible for activating methane at low temperatures. Increasing the vacancy concentration by appropriate doping at the A and B site was found to enhance the catalytic activity.

2:45 PM HH2.5

ELECTROLESS Pd AND Pt CATALYTIC ADDITION OF SnO₂ NANOPOWDERS. Raul Diaz, Fausto Sanz, Univ of Barcelona, Dept of Physical Chemistry, Barcelona, SPAIN; Albert Cirera, Albert Cornet, Joan R. Morante, Univ of Barcelona, Dept of Electronics, Barcelona, SPAIN.

A new method based on the electroless reduction of PdCl₂ and (NH₄)₂PtCl₄ is reported to produce catalytically added SnO₂ nanoscaled powders. The characterisation of these powders by means of XPS, ICP, Raman and XRD is discussed, showing the availability of the proposed catalytic addition mechanism, that can be a useful tool for the improvement of catalytic materials for gas sensors. Due to the fact that controlled catalytic addition of nanosized SnO₂ is essential to achieve the best possible sensitivity and selectivity for gas sensing applications, it is important to achieve highly reproducible techniques of catalytic addition at the lowest possible cost. Up to now the most important techniques used are: sol-gel, spray pyrolysis, CVD, dipping and sputtering. In this context the aim of the present paper is to present an alternative method to obtain catalytically added tin oxide and to control its properties avoiding some of the disadvantages shown by the other methods. Electroless metal deposition processes have been widely used since their introduction to provide metal coating of surfaces by simple immersion in a suitable aqueous solution. Its principles and behaviour are well established and, thus, metal deposition is obtained by reduction of metal ions present in the solution by means of a chemical reducing agent. The advantages of the proposed technique are: good stoichiometry achievement, mass production implementation facilities and low-cost production. Thereby, SnO₂ powders with Palladium and Platinum coming from a solution containing PdCl₂ and (NH₄)₂PtCl₄ respectively and deposited via electroless with Sn(II) acting as reductor are obtained. Different metal salt and reductor concentrations and different annealing temperatures are used to study their influence on the samples. The results show the presence of metallic Pd and Pt on the SnO₂ surface before annealing and the formation of PdO after annealing.

3:30 PM HH2.6

OXYGEN STORAGE CAPACITY AND LATTICE DEFECTS IN NANO-POWDERS OF CERIA AND CERIA-ZIRCONIA. Eugene Mamontov, Takeshi Egami, Univ. of Pennsylvania, Dept. of Materials Science and Engineering, Philadelphia, PA; Rasto Brezny, Manoj Koranne, W.R. Grace & Co.-Conn., Grace Davison Research, Columbia, MD.

The atomic structure of nano-crystalline powders of ceria, CeO₂, was studied by the pulsed neutron diffraction technique. Ceria-containing oxides are widely used as oxygen storage components in automotive catalytic converters. We found that the powders as prepared contained substantial amount of oxygen defects consisting of the oxygen interstitial ions in the octahedral sites and the oxygen vacancies in the tetrahedral sites of the cation sublattice. The concentration of vacancies was close to the concentration of interstitial ions, so the total oxygen stoichiometry was maintained. The oxygen defects annihilated at high temperature due to recombination of the interstitial ions with vacancies, and after the completion of the thermal cycle only a small fraction of the defects was retained. The results of our structural analysis and the temperature-programmed reduction measurements performed on thermally aged samples for the first time establish a direct link between the concentration of oxygen defects in nano-powders of ceria and their oxygen storage capacity. The surface area of the samples, on the other hand, exhibits much less correlation with the oxygen storage capacity. It is suggested that oxygen defects are the source of oxygen storage capacity in ceria-based catalyst supports, and the preservation of oxygen defects is critical for the stability of the oxygen storage properties against thermal aging. The results of comparative studies of CeO₂ and (Ce,Zr)O₂ solid-solution nano-powders using pulsed neutron diffraction and temperature-programmed reduction will be discussed.

3:45 PM HH2.7

DISPERSED CATION/ANION MODIFIED Pt-PROMOTED CERIA-ZIRCONIA SOLID SOLUTIONS AS CATALYSTS OF METHANE OXIDATION INTO SYNGAS BY WATER IN REVERSIBLE REDOX CYCLES. Erhard Kemnitz, Institute for Chemistry, Humboldt-Univ, Berlin, GERMANY; Vladislav A. Sadykov, S.A. Veniaminov, D.I. Kochubei, B.N. Novgorodov, T.G. Kuznetsova, E.B. Burgina, S.V. Tsybuluya, E.A. Paukshitis, Borekov Institute of Catalysis SB RAS, Novosibirsk, RUSSIA; S.A. Beloshapkin, Novosibirsk State University, Novosibirsk, RUSSIA; V.V. Lunin, Chemical Dep. of Moscow State Univ., Moscow, RUSSIA; A. Aboukais, Lab. de Catalyse et Environnement MREID, Univ. du Littoral- Cote d'Opale, Dunkerque, FRANCE.

Syngas generation via methane oxidation by the oxides lattice oxygen is a very attractive option. However, this approach is not yet realized

in practice due to sintering of oxides in red-ox cycles at enhanced temperatures required to ensure a rapid oxygen diffusion from the bulk. In this work, ceria-zirconia system known for a good oxygen storage capacity was chosen as basic, and fluorine/calcium insertion was used to improve the lattice stability in the red-ox cycles. Pechini method ensuring homogeneous chemical composition of complex oxides was chosen for the synthesis of samples with specific surface area exceeding 20 m²/g after annealing at 700°C. For the efficient methane activation, the samples surface was modified by Pt (0.2wt.%) introduced via the wet impregnation. The bulk structure of samples was characterized by XPD, EXAFS and FTIRS of lattice modes. Specific reactivity of surface oxygen, its amount, coefficients of bulk and near-surface diffusion as dependent upon the samples composition and temperature were estimated using samples reduction by CO in pulse/flow regimes and dynamic thermal oxygen isotope exchange. Insertion of fluorine into the lattice results in decreasing the degree of oxygen polyhedra distortion, thus decreasing the amount of reactive oxygen and diffusion coefficients, while calcium and Pt addition counteracts this effect. Even at moderate (500°C) temperatures, for Ca-F-Pt modified Ce-Zr sample, this reactive oxygen (up to 5 monolayers) is easily removed by methane generating CO and hydrogen with a high selectivity. Samples reoxidation by water at the same temperature restores the oxygen capacity producing more hydrogen. Repeated redox cycles do not deteriorate the samples performance. Hence, modified ceria-zirconia based systems elaborated in this work were shown to be efficient catalysts of methane conversion into CO and hydrogen in the unsteady-state conditions of redox cycles promising for the practical application. This work is in part supported by RFBR -INTAS grant No IR-97-402.

SESSION HH3: CATALYTIC TESTING AND ANALYSIS I

Chairs: Andreas Stein and Gene S. Smotkin
Wednesday Afternoon, November 29, 2000
Room 201 (Hynes)

4:00 PM HH3.1

DEVELOPMENT OF A REAL-TIME MONITORING PROCESS OF THE MICROSTRUCTURE AND STOICHIOMETRY OF CERIUM OXIDE THIN FILMS PRODUCED BY ELECTRON BEAM EVAPORATION. P. Patsalas, S. Logothetidis, Ch. Metaxa, Aristotle Univ, Dept of Physics, Thessaloniki, GREECE.

Cerium Oxide (CeO₂) or Ceria is a rare-earth oxide that is used for various catalytic and optical applications. For all applications, non-destructive, in-situ and real time monitoring of Ceria films microstructure and stoichiometry during deposition is of vital importance to tailor desired properties. In this work we present a combined Ellipsometric and X-ray study of Ceria films' microstructure and stoichiometry in an effort to develop such an intelligent, real-time monitoring process of the Ceria deposition by e-beam evaporation. Spectroscopic Ellipsometry, a non-destructive optical characterization technique, was employed to study the Ceria films optical properties and electronic structure in the energy region 1.5-5.5 eV. The interference phenomena occurring due to the optical transparency of Ceria films are used to monitor the film thickness and deposition rate. The optical properties (refractive index in the visible energy region, mean optical absorption and fundamental gap) are strongly correlated with the Ceria films microstructure as it was studied by X-ray Diffraction (XRD) and Reflectivity (XRR). Changing the deposition rate and substrate temperature has varied the Ceria films' microstructural characteristics (grain size, orientation, density and voids content). XRD revealed the fluorite structure of the films in all cases. The cell size of Ceria films was found the same with the one of the bulk Ceria indicating that the internal stresses in the films are very low. It was found a linear increase in mean grain size of the Ceria films and a reorientation from the (111) to the (200) crystallographic direction with substrate temperature. This reorientation is explained following simple thermodynamic considerations. The film density measured by XRR, increases with substrate temperature as well. The voids content of the films were calculated from the film density, taking into account the density of the bulk Ceria and it was correlated with the monitored refractive index.

4:15 PM HH3.2

IN-SITU ULTRAVIOLET RAMAN SPECTROSCOPY OF ADVANCED CATALYSTS. Joel W. Ager III, Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA; Craig Tewell and Gabor Somorjai, Materials Sciences Division, Lawrence Berkeley National Laboratory and Department of Chemistry, University of California at Berkeley, Berkeley, CA; Federica Malizia, Montell Research, Ferrara, ITALY.

An ultraviolet Raman spectroscopy system has been developed for the *in-situ* and *ex-situ* study of high-surface area, microporous catalysts.

Use of ultraviolet excitation at 244 nm is used to suppress fluorescence interference that has previously limited the application of Raman spectroscopy to catalysis studies. *In-situ* studies are performed in both packed bed and fluidized bed reactors at reaction temperatures up to 250°C. Quantitative measurement of reactants and products via auto-sampling gas chromatography is performed simultaneously with the spectroscopic analysis. Initial results on the effect of H₂ on the dehydration of Al₂O₃·3H₂O at 250°C will be presented. Results from the *ex-situ* study of MgCl₂tOH_x (0 ≤ x ≤ 6), which is a precursor to the support for the Ziegler-Natta catalyst, will be presented. Changes in the UV-Raman spectrum between 100 and 300 cm⁻¹ as a function of ethanol loading will be related to the structure of the MgCl₂-ethanol complex. In an initial *in-situ* study of a catalyzed reaction, cyclohexene disproportionation on Pt/Al₂O₃ was studied between 0 and 125°C while the cyclohexane/benzene product ratio was measured continuously. Correlations between the vibrational spectra of surface species and the catalyst performance and deactivation will be discussed.

4:30 PM HH3.3

ATOMIC RESOLUTION Z-CONTRAST IMAGING AND EELS ANALYSIS OF SUPPORTED HETEROGENEOUS CATALYST SYSTEMS. I.A. Rauf, K. Sun, and N.D. Browning Department of Physics, University of Illinois at Chicago, Chicago, IL.

Understanding of the interactions of nanometer sized catalytic metal particles with their support and its effect on the degradation mechanism is of practical significance. Atomic resolution transmission electron microscopy images are usually difficult to interpret and do not contain information about the local chemistry. Atomic-resolution Z-contrast imaging in combination with electron energy loss spectroscopy in a scanning transmission electron microscope (STEM) is emerging as a powerful technique for analyzing such systems. We have studied four different catalyst systems using this technique; namely Pt/SiO₂, Pt-Fe/Al₂O₃, Pt/KL-zeolite and Sb/SnO₂. Results of detailed microstructural and chemical analyses of these particles will be presented. Usefulness of above techniques to study such systems will be established. Our results indicate that very small particles tend to adopt strained host structure. As the particle size increases, the core of the particles adopts its own structure with an amorphous layer at the periphery. EELS data indicates that Pt particles do not form a bond to the support oxide but are merely adsorbed to it.

SESSION HH4: POSTER SESSION
Wednesday Evening, November 29, 2000
8:00 PM
Exhibition Hall D (Hynes)

HH4.1

ELECTROCATALYTIC PROPERTIES OF PLATINUM-CONTAINED COATINGS ON CARBON MATERIALS. V.V. Poplavsky, V.G. Matys, I.M. Zharsky, Belarussian State University of Technology, Minsk, BELARUS.

Electrocatalytic properties of ion assisted deposited coatings on graphite and glassy carbon electrodes have been investigated. The coatings were formed by deposition on carbon plates of one or sequentially two different metals. Platinum was deposited directly upon the carbon substrate. Other metals such as Ag, Ni, Co, Pb were deposited over platinum. Metals deposition was carried out with pulsed arc plasma under accelerated voltage 20 kV. The RBS and XPS methods were used for investigations of the coatings. Content of each metal in the deposited layers was ~10¹⁶-10¹⁷ atom/cm²; coating thickness comprised ~50-200 nm. Electro-catalytic activities of the platinum coating and of each among such bimetallic coatings in the hydrogen evolution reaction for different carbon substrates have been studied. Deposition of platinum on carbon substrate results in significant increase in activity. Electrocatalytic activity of bimetallic coatings was comparable to activity of platinum and was significantly higher than activity of the above deposited metal. It may be concluded that a relatively thick layer takes part in electrochemical process of hydrogen ions reduction. However, activities of bimetallic coatings do not correlate with activity of pure metals in the studied electrocatalytic reaction. So, in case graphite substrate is treated, the activity drops in the range Co>Pb>Ni>Ag, in case glassy carbon is exposed to deposition - in the range Ag≈Co>Ni≈Pb, and regarding pure metals - in the range Ni>Co>Ag>Pb. Deposition of Co over Pt does not influence activity of the platinum coating. Deposition of Ag reduces activity within glassy carbon substrate and does not influence as regards graphite substrate; deposition of Pb has the contrary effect. Deposition of Ni decreases activity in case of both carbon substrates. Interaction of deposited metals with carbon substrate and interaction between deposited metals in surface layer may be significant and influence electrocatalytic activity of the studied bimetallic coatings.

HH4.2

TUNABLE HETEROGENEOUS CATALYSIS IN CUBIC ALUMINAS. Karl Sohlberg, Department of Chemistry, Drexel University, Philadelphia, PA; Stephen J. Pennycook; Solid State Division, Oak Ridge National Laboratory, Oak Ridge, TN; Sokrates T. Pantelides, Department of Physics and Astronomy, Vanderbilt University, Nashville, TN.

The surfaces of the γ and η forms of alumina are well known to differ significantly in acidity, and correspondingly in catalytic activity. This difference in chemical properties is remarkable because the two forms are very similar in bulk structure. Both forms have a defect spinel structure, differing essentially only in the distribution of bulk point defects. In some historical instances the γ and η forms have even been considered identical. Despite the close similarity of the bulk structures, however, surface reconstructions observed on γ- and η-alumina are qualitatively different. Here we demonstrate through first principles calculations that subtle differences in the bulk point defect distribution between these two forms of alumina give rise to the major differences in the mode of surface reconstruction, and are the origin of the different levels of acidity. These results evince a surface catalytic activity of alumina that can be tuned by manipulating the bulk point defect distribution to switch between the two modes of surface reconstruction.

HH4.3

FORMATION OF THE FRENKEL-TYPE OXYGEN DEFECTS IN PRE-TREATED SINGLE CRYSTALS OF CERIA. Eugene Mamontov, Takeshi Egami, Univ. of Pennsylvania, Dept. of Materials Science and Engineering, Philadelphia, PA; Manoj Koranne, Rasto Brezny, Michael Juskelis, W.R. Grace & Co.-Conn., Grace Davison Research, Columbia, MD.

Ceria, CeO₂, and ceria-containing oxides are widely used as oxygen storage components in automotive exhaust catalysis. Recently we observed the Frenkel-type vacancy-interstitial oxygen defects in ceria powders and proposed that they may be a prerequisite for the catalytic activity of ceria at moderate temperatures [1]. We also suggested that the presence of such defects may be common in all forms of ceria, including single crystals. We have studied the structure of two single crystals of CeO₂ using the time-of-flight neutron scattering technique. One of the crystals was annealed at 1473 K in air, whereas the other was reduced to the composition of CeO_{1.84} and then re-oxidized back to CeO₂ at low temperature. The structural analysis showed approximately 1 % concentration of the Frenkel-type oxygen defects in the single crystal that has undergone the reducing and re-oxidizing treatment, while no defects were found in the other single crystal of ceria. This is in agreement with our previous suggestion [1] that the Frenkel-type defects in ceria may form during sample processing. The difference in the concentration of the oxygen defects in single crystals and catalytically active nano-powders of ceria will be discussed.

[1] E. Mamontov, T. Egami, J. Phys. Chem. Solids 61, 1345 (2000).

HH4.4

CATALYTIC EFFECT OF GALLIUM ELECTROLYTE ADDITIVES ON ALUMINUM ACTIVATION IN ALUMINUM SEMI-FUEL CELLS. Louis G. Carreiro, Steven P. Tucker, Maria G. Medeiros, Delmas W. Atwater, Naval Undersea Warfare Center, Newport, RI; Craig M. Deschenes, BAE Systems, Middletown, RI; Christopher N. LaFratta, Dept of Chemistry, Univ of Mass/Dartmouth, Dartmouth, MA.

The aluminum semi-fuel cell (Al-SFC) represents an alternative energy source for undersea vehicle power and propulsion applications. Similar in principle to the operation of a battery, an Al-SFC utilizes an aluminum metal anode together with a liquid cathode (hydrogen peroxide) in the electrochemical generation of power. The effectiveness of the SFC depends in part on the sustained reaction of the aluminum anode with a caustic electrolyte solution. However, in caustic media (such as sodium hydroxide) aluminum metal tends to form a passive oxide layer that can reduce its chemical reactivity. This study explores the use of various gallium electrolyte additives that prevent/inhibit oxide-layer formation, hence act as catalysts for the activation of aluminum. It was found that addition of gallium ion to the anode electrolyte affects the rate of both the electrochemical reaction of aluminum to form sodium aluminate and the corrosion reaction of aluminum to produce hydrogen gas. At low gallium concentrations (less than 2.0 x 10⁻⁵ M), the corrosion reaction is sufficiently suppressed and the electrochemical oxidation of aluminum occurs with relatively high efficiency (greater than 80%). Al-SFC full-cell test data will show that gallium addition to the solution electrolyte enhances aluminum activity and results in increased cell voltages.

HH4.5

ELECTROCATALYTIC PROPERTIES OF CORE-SHELL GOLD

AND ALLOY NANOPARTICLE ASSEMBLIES. Yongbing Lou, Mathew M. Maye and Chuan-Jian Zhong, Department of Chemistry, State University of New York at Binghamton, Binghamton, NY.

Metal or oxide particles in the nanometer-sized range are emerging as attractive candidates for use as highly effective catalysts in fuel cell technology. The catalytic activity can be exploited in the form of interfacial assembly, but a key challenge is the effective isolation of the nanosized properties while retaining the catalytic properties. Core-shell nanoparticles provide an intriguing pathway because the encapsulating structure may allow the manipulation of core size properties and enhancement of the stability of nanosized catalysts against aggregation propensity. This paper presents results of an investigation of the catalytic properties of such nanoparticles with single or alloyed core composition such as gold, gold-silver and gold-platinum. The nanoparticles are capped with thiolates in a network thin film on electrode via covalent bonding at inter-core sites or hydrogen-bonding at inter-shell sites. It is demonstrated that the capped nanosites can be both electrochemically-accessible and catalytically-active to the oxidation of carbon monoxide and related hydrocarbons depending on a number of factors including core size, shape, composition, molecular capping and potential polarization-induced activation. Electrochemical and scanning probe microscopic results will be presented, along with discussions on tailoring strategies of the nanosized gold and alloy catalysts via core-shell chemical manipulation.

HH4.6

Pt-METAL OXIDE AEROGEL CATALYSTS: CHARACTERIZATION BY X-RAY PHOTOEMISSION SPECTROSCOPY. A.J. Nelson and John G. Reynolds, Lawrence Livermore National Laboratory, Livermore, CA.

X-ray photoemission spectroscopy was used to study Pt-metal oxide aerogel catalysts that have been developed to respond to increased NO_x emissions of lean-burn engines. Lean-burn engines, critical components of low and zero emission vehicles, can produce much higher levels of engine-out NO_x and current three-way catalytic converters are not sufficient to meet Clean Air Act standards. Platinum catalysts were formed by the reaction of modified Pt coordination compounds with selected transition-metal alkoxides through sol-gel techniques into aerogels. Photoemission measurements on the valence band electronic structure and Pt 4f, Si 2p, Ti 2p and O 1s core lines were used to evaluate the chemistry of the material after each processing step. Results indicate Pt-O bonding and reduced Pt dispersed in the aerogel. In addition, Si 2p, Ti 2p and O 1s binding energies indicate an oxo-bridged network structure. This work was performed under the auspices of the U.S. Department of Energy by University of California Lawrence Livermore National Laboratory under contract No. W-7405-ENG-48.

HH4.7

HIGHLY SELECTIVE HYDROGENOLYSIS REACTIONS USING NOVEL NANOSTRUCTURED PALLADIUM CATALYSTS. Suyoung Ryoo, Hongkyu Kang, Hee Yoon Lee, Jinwoo Cheon, Korea Advanced Institute of Science and Technology (KAIST), Department of Chemistry and School of Molecular Science, Taejeon, KOREA.

In this report, we describe the preparation of well-defined ball shaped Pd nanomaterials inside a cubic phase MCM-48 matrix and its catalytic activities. Pd was chosen because it is an important and versatile catalyst for many inorganic and organic reactions. Nanostructured Pd@MCM-48 catalysts are prepared by chemical vapor infiltration into the template matrix MCM-48, followed by mild thermal decomposition to generate Pd metal inside the template. Pd@MCM-48 with ~ 6 wt % Pd loading produces singular or multiply agglomerated golf ball shaped Pd domains 30~40 nm in diameter. Energy dispersive X-ray analysis and TEM confirms the presence of Pd contents inside the matrix. By using this nanostructured Pd@MCM-48 as a catalyst, a highly selective hydrogenolysis reaction to deprotect benzylether that is used to protect alcohol groups in unsaturated organic molecules is carried out. We found interesting chemoselectivity where only hydrogenolysis of benzylether proceeds and no hydrogenation of the double bond occurs in the molecule. Conventional Pd catalysts did not show such chemoselectivity. Our Pd nanocatalyst is air stable and reusable by filtration and can possibly be extended to other types of organic reactions

HH4.8

PREPARATION OF UNIAXIALLY ALIGNED TiO₂ TUBES USING ORIENTATION CONTROLLED ORGANIC FIBERS AS TEMPLATES. Atsushi Hozumi, Yoshiyuki Yokogawa, Tetsuya Kameyama, National Industrial Research Institute of Nagoya, Ceramics Technology Department, Bioceramics Laboratory, Nagoya, JAPAN; Tomohito Ito, Toba National College of Maritime Technology, Department of Maritime Technology, Mie, JAPAN.

Porous materials prepared with the use of various kinds of templates, such as surfactant molecules, block copolymers and emulsions etc. have excellent potential for a wide variety of advanced applications. In such a circumstance, pore size control in micrometer-order as well as in nanometer-order is of crucial importance. Among various templates, the use of organic fibers around micrometer in diameter is one of the promising ways to obtain such a larger pore. Here we report a simple procedure to prepare uniaxially aligned TiO₂ tubes with a micrometer-size hollow. This technique is based on the orientation control of the organic fibers, that is, silk fibers using an electrostatic means. In this study, short silk fibers cut from silk thread were used. They were about 1 mm and 15 μm in length and thickness, respectively. First, these fibers were dispersed into insulating liquid and this suspension was fed to the apparatus. Next, a dc voltage of 12 kV was applied between the two electrodes. The suspended fibers were electrostatically oriented to the electric field direction and were collected on a paper filter to obtain a mat. Subsequently, the mat was immersed in a precursor solution prepared with tetra-n-butyl orthotitanate, dehydrated ethanol and acetylacetone. After immersion, they were dried in an oven maintained at 343 K for 0.5 h. Finally, the silk fibers were eliminated by calcination for 1 h at 923 K in air. As confirmed by an optical microscope, the calcined fibers were also uniaxially aligned. However, large volume shrinkage of the fibers was observed. According to SEM observation, the fibers formed into tube-like shapes and their average diameters of the hollows were about 2 μm. The XRD patterns indicated that the tube materials were anatase type titania. These uniaxially oriented TiO₂ tubes are applicable to photo-catalyst filters with lower air or fluid pressure loss.

HH4.9

PREPARATION OF V₂O₅-TiO₂ CATALYST FIBERS AND THEIR STRUCTURAL PROPERTIES AND CATALYTIC BEHAVIOR. Yasuyuki Oki, Hironobu Koike, Yoshiaki Takeuchi, Hiroyuki Ando, Tatsuya Suzuki, Basic Chemicals Research Laboratory, Sumitomo Chemical Co., Ltd., Ehime, JAPAN.

Continuous Catalyst fibers composed of V₂O₅ and TiO₂ were prepared from polymerized material which was synthesized through hydrolysis and polymerization reaction by adding a controlled amount of water to the solution of partially chelated titanium alkoxide and vanadium alkoxide. The concentrated viscous solution of the polymerized material which had good spinability was extruded through a nozzle having a diameter of 50 μm and then precursor fibers were obtained. The resulting precursor fibers were treated with water vapor and then calcined to form continuous catalyst fibers having an average diameter of 25 μm per monofilament. The catalyst fibers exhibited favorable structural properties (large specific surface area of more than 200 m²/g and large pore volume of more than 0.20 cm³/g) and capability to stabilize V₂O₅ in a well dispersed form up to high loading. No agglomerate V₂O₅ was observed on the surface and inside the fiber up to 27% by weight based on the catalyst fiber. V/Ti mole ratio of the fiber was constant at all parts of the fiber and the species of V₂O₅ on the surface of TiO₂ (anatase) having a crystallite size of 5-10 nm formed the thin layer. The catalyst fibers had high activity in reduction of NO by NH₃ and decomposition of organic chlorine compounds.

HH4.10

OXIDATIVE DEHYDROGENATION OF PROPANE AT SHORT CONTACT TIMES OVER MONOLITHIC SUPPORTED OXIDE AND COMPLEX FRAMEWORK ZIRCONIUM PHOSPHATE CATALYSTS. Vladislav A. Sadykov, S.N. Pavlova, N.F. Saputina, A.V. Simakov, N.N. Sazonova, I.A. Zolotarskii, V.A. Kuzmin, A.N. Salanov, V.P. Ivanov, D.I. Kochubei, V.V. Kriventsov, E.A. Paukshtis, E.B. Burgina, V. Rogov, Boreskov Inst. of Catalysis SB RAS, Novosibirsk, RUSSIA; Yu. V. Frolova, Novosibirsk State Univ, Novosibirsk, RUSSIA; R. Roy, D.K. Agrawal, Materials Research Lab, Penn State Univ, University Park, PA.

New types of active components supported on corundum micromonoliths including sulfated V-Mg oxide system and complex framework zirconium phosphates were tested in the propane oxidative dehydrogenation at short contact times. Their acid-base and red-ox properties were modified by variation of the nature and content of transition metal (Mn, Co, Ce, Sn, V) and alkaline/alkaline-earth cations introduced into the lattice. TEM, XRD, EXAFS and FTIRS were used to characterize their bulk structure, while surface composition, texture and redox/acid properties were studied by SIMS, SEM, TPR, FTIRS of the surface hydroxyls and adsorbed CO. Samples were tested both in the isothermal mode in diluted mixtures and in the autothermal mode at high concentrations of propane in air. In isothermal experiments, in the presence of oxygen, primary selectivities to propylene for some compositions were found to be very high, being dependent upon the redox and acid properties of the surface. In the autothermal experiments, all oxygen is consumed within the narrow inlet part of monolith due to deep oxidation of propane increasing thus temperature up to 11000 C. For predominant

part of the monolith length, the endothermic propane dehydrogenation in the presence of water and carbon dioxide occurs. Framework zirconium phosphates even without Pt promotion are able to keep the process in the autothermal mode, functioning as efficient oxidation catalysts in the inlet part of monolithic layer and as thermally stable dehydrogenation catalysts not subjected to coking in the middle and end parts of the layer. By using simultaneous tuning of the feed composition, temperature profile along the monolith layer and its spatial design, the yield of propylene in the autothermal mode was increased as compared with earlier reported values for propane oxidative dehydrogenation at short contact time on Pt supported catalysts.

Financial support of Engelhard Corp. is gratefully acknowledged.

HH4.11

CONTROL OF THE PORE STRUCTURE OF SUPPORTS BASED UPON ALUMINA/ALUMINUM COMPOSITES PREPARED BY HYDROTHERMAL OXIDATION OF ALUMINUM POWDER. Sergei F. Tikhov, Yulia V. Potapova, Vladislav A. Sadykov, V.B. Fenelonov, S.V. Tsybulya, A.N. Salanov, V.T. Yakushko, G.S. Litvak, L.F. Melgunova, Boreskov Inst. Of Catalysis SB RAS, Novosibirsk, RUSSIA.

Hydrothermal oxidation of aluminum powder mixed with various oxide additives and placed in a confined volume followed by decomposition of obtained hydroxides is known to produce compact mechanically strong highly porous composites of various shapes promising as supports or catalysts for different applications. In this work, the effect of such oxide additives as CaO, MgO, lanthana, titania and alumina on the process of composite formation and its pore structure has been studied in details. Oxide additives were found to affect appreciably the reactivity of aluminum particles in the course of hydrothermal oxidation, as well as the features of hydroxides decomposition. The analysis of the nitrogen adsorption/desorption isotherms with the help of comparative method combined with SEM and thermal analysis allowed to obtain a detailed description of the pore structure and elucidate the effect of oxide additives on its formation. Composites were revealed to have a developed microporosity, while containing simultaneously a great fraction (more than 50%) of ultramacropores. A general relation between the mean particle size of precursors powders, total pore volume and crushing strength was established. This work is in part supported by RFBR 99-03-32853 grant.

HH4.12

A NOVEL CATALYST PREPARATION FOR DECHLORINATION OF CHLORINATED HYDROCARBONS. Young Sung Cho, Jong Chul Park, Byung Hwan Lee, Jongheop Yi, School of Chemical Engineering, Seoul National University, Shillim-dong, Kwanak-gu, Seoul, S KOREA.

Catalytic dechlorination is recognized as a promising recycling process for the treatment of chlorinated hydrocarbons, produced as a waste and by-products. However, conventional dechlorination catalysts are based on hydrodechlorination mechanism and produce paraffin series and hydrochloric acid rather than useful olefin series. Therefore, it is required to develop dechlorination catalysts to produce olefin series. In this study, as a model system, dechlorination of trichloroethane was selected. Mesoporous molecular sieves have been attracted much attention as a catalyst support since the introduction of MCM-41. They have opened up opportunities of new catalysts with desirable catalytic properties, such as large surface area, well arranged pore array, and controlled pore size. In addition to these desirable catalytic properties, mesoporous silica is easily functionalized with retaining the mesoporosity. This property was utilized to synthesize finely dispersed Ni catalysts on mesoporous silica for dechlorination of trichloroethane. In this study, in the first step, mesoporous silicas were prepared by using poly(alkylene)oxide triblock copolymers (Pluronic P123 and P103, BASF) as templates and tetraethoxy silane as a silica precursor. The mesoporous silicas synthesized have highly ordered structures with pore diameter of 8.5 nm. In the second step, hybrid mesoporous silica were synthesized by grafting various silane groups onto the synthesized mesoporous silicas. 3-aminopropyltriethoxy silane, 3-mercaptopropyltrimethoxy silane, and ethylenediaminetriacetic acid salt were grafted onto mesoporous silica by refluxing in dry toluene under a nitrogen flow condition. Also, after grafting 3-iodopropyltriethoxy silane, 2-hydroxy-5-nonyl-acetophenoneoxime or glycine salt was incorporated onto the surface of synthesized mesoporous silica. The mesoporous silicas adsorbed Ni molecules under the pH-controlled solution. Finely dispersed Ni catalyst was obtained by mild oxidation of organic groups. After silanization and immobilization of ligand group, it was observed that BET surface area of hybrid mesoporous silica was decreased from 770 m²/g to 280 m²/g and pore diameter was decreased by 2nm. TPR and H₂ chemisorption experiments were performed to evaluate the metal dispersion of these catalysts. In addition, SAXS, TEM, and ICP were used to characterize the synthesized Ni catalysts, and investigate the effect of surface characteristics on the catalytic performance.

HH4.13

EXPERIMENTAL SYSTEM TO STUDY CATALYSIS IN MICRO-GEOMETRY. S. Ouyang, M. Prevot, H. Surangaliker, W. Yang and R.S. Besser, Louisiana Tech Univ, Dept of Chemical Engineering and Institute for Micromanufacturing, Ruston, LA.

Microreactors offer many capabilities for catalytic reactions such as a wide range of microreactor types, the ability to employ different catalysts, tight control of reactions, and rapid characterization of the reaction. We have constructed an experimental setup that permits microreactors to be characterized for reaction conversion and selectivity over a wide range of operating conditions. Ultimately, we wish to use this setup to test the microreactors fabricated in our lab for industrially important reactions. This information will be useful for developing new catalysts for maximum conversion and optimum cost. In a characterization experiment, the microreactor is positioned in a heated test block. The reactor parameters are measured using thermocouples, flow rate meters, and pressure transducers. These measurements, taken as analog signals, are changed to digital signals by computer input and output boards. The program LABVIEW (TM) is used to read these parameters and to maintain their values by feedback control. The controlled flow of gas is allowed to pass through the microchannels of the microreactor, which are coated with a thin-film catalyst. The microreactors are easily replaceable, and the setup allows for quick analysis of the reaction products through a quadrupole mass spectrometer. Thus the activities of various catalysts can be compared and the most efficient catalyst identified. We will present the details of the experimental system and the results of model reactions characterized in the system.

HH4.14

ELECTRONIC STRUCTURE OF THE TITANIUM SITE IN TITANIA SILICALITE (TS-1) CATALYSTS. Allison S. Sout, A.E. Stiegman, Department of Chemistry, Florida State University, Tallahassee, FL.

Titanium-Silicalite (TS-1) is an interesting and commercially useful heterogeneous oxidation catalyst that utilizes hydrogen peroxide to accomplish the selective oxidation of, for example, phenol. An area of particular interest with regard to these materials is the coordination geometry and electronic structure of the titanium site as it resides in the silicalite matrix. To this end electronic spectroscopy, collected as diffuse reflectance spectra of the powdered solids, has often been used to support the assignment of a tetrahedral structure for the titanium site. Luminescence spectroscopy has identified emission from the titanium site occurring at 490 nm. The emission is a long-lived (80 microseconds) phosphorescence which shows a vibronic progression in the 960 cm⁻¹ associated with the known Ti-O-Si stretch. Emission excitation spectra show that, contrary to previous assertions, the titanium site has electronic absorption in the range of 30,000-42000 cm⁻¹. This suggests that electronic spectroscopy does not support tetrahedral substitution in the case of TS-1.

HH4.15

CATALYTIC OXIDATION OF CO OVER COMBUSTION SYNTHESIZED Cu SUBSTITUTED MnAl₂O₄ SPINEL CATALYST. A.S. Prakash, M.S. Hegde, Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore, INDIA; A.M.A. Khader, Dept. of Chemistry, Mangalore University, Mangalore, INDIA.

The catalytic oxidation of CO has been carried out over combustion synthesized MnCu_xAl_{2-x}O₄ (x=0 to 1) catalyst using temperature programmed reaction (TPR) technique in a packed bed tubular reactor. Catalytic activity increases with copper content, and shows maximum activity for MnCu_{0.75}Al_{1.75}O₄. Which exhibits a complete CO oxidation below 75°C. The catalyst have been characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM) and X-photoelectron spectroscopy (XPS) studies.

HH4.16

TOOTH BLEACHING WITH TiO₂ PHOTOCATALYST. Toru Nonami, Hiroshi Taoda, Takuro Ishibashi, Kouzou Ishibashi, National Industrial Research Institute of Nagoya, JAPAN.

A titanium dioxide photocatalyst produces vital oxygen, OH radicals, and other species by exposure to light. This action allows ready decomposition of various organic chemical substances normally difficult to decompose. Titanium dioxide is thus believed to function effectively in decomposition of dental colorants, with potential application as a dental bleaching agent. To establish a method for safe, simple, and expeditious tooth bleaching using titanium dioxide, we studied the potential for use of titanium dioxide as a dental bleaching agent by applying a dilute, blended solution of hydrogen peroxide and titanium dioxide to the surface of extracted, discolored teeth; providing light irradiation; and observing changes in the coloration and other aspects of the teeth. All teeth demonstrated an effect from roughly 10-30 minutes bleaching. To investigate

bleaching-induced change in the properties of the enamel, the microstructure of the tooth enamel was also observed before and after bleaching, and the results showed virtually no change.

HH4.17

LOW TEMPERATURE OLEFIN ISOMERIZATION REACTIONS AT PEM FUEL CELL/Pd/NaFION CATHODES. Lloyd Ploense, Maria Salazar, E.S. Smotkin, Department of Chemical Engineering, Illinois Institute of Technology, IL.

We recently reported the electrochemical promotion of the heterogeneously catalyzed isomerization of 1-butene to cis- and trans-butene at the remarkable low temperature of 70°C at a fuel cell cathode using Nafion as the electrolyte. This was the first reported case of a NEMCA promoted unimolecular and non-redox reaction concomitant with the reduction of butene to butane. We now present isotopic mass spectral and FTIR data confirming the mechanism involves abstraction of a proton from the catalytic surface for Markovnikov addition to the C-1 carbon concomitant with removal of a proton from C-3 to yield the isomer. We also demonstrate that electrochemical promotion also enhances carbon-carbon bond migrations. The isomerization of olefins on polymer supported catalysts demonstrates that an ionomeric polymer can substitute for inorganic acidic supports in acid catalyzed reactions on metal surfaces.

HH4.18

SYNTHESIS OF POROUS PEROVSKITE OXIDE FOR NO_x DECOMPOSITION. Takao Kanai, Kazuyuki Matsuda, Fine Ceramics Research Association, Synergy Ceramics Laboratory, Nagoya, JAPAN; Masanobu Awano, National Industrial Research Institute of Nagoya, Nagoya, JAPAN; Kunihiro Maeda, Fine Ceramics Research Association, Synergy Ceramics Laboratory, Nagoya, JAPAN.

A composite device for decomposition of NO_x to N₂ and O₂, which consists of a catalyst for selective adsorption and decomposition of NO_x and a solid electrolyte for oxygen pumping, has been investigated. Some perovskite oxides, for example, Sr-doped LaCoO₃ were examined as the catalytic materials. In this paper, porous perovskite oxide films were synthesized by wet-chemical process using urea and the characteristics were investigated. In the case of Sr-doped LaCoO₃, single phase of La_{1-x}Sr_xCoO₃ (X=0.2, 0.4) was formed after heat treatment above 600°C. Electrical conductivity at room temperature depended on the heat treatment temperature and the maximum value over 1 10³ S/m was obtained for the specimen heated at 800°C. The ability of NO_x removal in a mixed gas was investigated for synthetic conditions and microstructure, especially pore structure.

HH4.19

GRAIN GROWTH IN THREE-Dimensionally ORDERED MACROPOROUS (3DOM) MATERIALS AS OBSERVED IN THE TEM. Christopher F. Blanford, Hongwei Yan, Rick C. Schroden, Mohammed Al-Daous, Andreas Stein, Univ of Minnesota, Dept of Chemistry, Minneapolis, MN; C. Barry Carter, Univ of Minnesota, Dept of Chemical Engineering and Materials Science, Minneapolis, MN.

Three-dimensionally ordered macroporous ("3DOM") materials have been synthesized from latex colloidal crystal templates and solutions of either metal alkoxides or metal salts. The products feature a large and highly accessible surface, suggesting that they are suitable as catalysts or catalyst supports. In order to evaluate the suitability of these materials for such applications, samples of metal and metal oxide 3DOM materials and a sample of tungstosilicate clusters grafted on 3DOM silica were investigated by high-temperature transmission electron microscopy (TEM). The observed grain growth and morphological changes will help establish the maximum operating temperature at which these materials are stable. The results of these in situ experiments were compared to samples heated ex situ then observed by TEM.

SESSION HH5: CATALYTIC TESTING AND ANALYSIS II

Chairs: Douglas L. Gin and Dick A. Nagaki
Thursday Morning, November 30, 2000
Room 201 (Hynes)

8:30 AM *HH5.1

HIGH-SPEED EXPERIMENTATION & SIMULATION: A PARADIGM SHIFT IN CATALYST AND PROCESS R&D. Ian E. Maxwell, Avantium Technologies BV, Amsterdam, THE NETHERLANDS.

Integrated high-speed experimentation & simulation (HSE&S) technology can be described as a combination of enabling technologies that are deployed to screen for new catalysts and/or processes at high throughput rates by integrating the use of robotic synthesis, reactor

miniaturization, parallelism, high speed functionality techniques and informatics/simulation. Clearly, this approach has the potential for enormous time savings in research and development, thus enabling industry to bring new catalysts and processes on to the market at lower cost and, more importantly, dramatically shorten the development time. It also increases the chances of technical success and innovation through greater parameter diversity in the catalyst/process screening phase.

It is thus not inconceivable that HSE&S technology will create a new paradigm in research and development methodologies for many sectors of industry and can therefore be considered as "game-changing technology".

Some examples will be given of the development of HSE&S technologies and the application for rapid experimentation of heterogeneous, homogeneous and polymer catalyst systems. In addition, some future opportunities and challenges in this exciting new field will be discussed.

9:00 AM HH5.2

MICROREACTION TECHNOLOGY FOR EFFICIENT DISCOVERY OF NEW CATALYST MATERIALS. R.S. Besser, S. Ouyang, M. Prevot, H. Surangalihar and W. Yang, Louisiana Tech University, Department of Chemical Engineering and Institute for Micromanufacturing, Ruston, LA.

Microreaction devices are miniature chemical systems resembling electronic chips in appearance. They are fabricated using micromachining techniques that originated in microelectronics and evolved further in the field of microelectromechanical systems (MEMS). Having characteristic dimensions on the order of micrometers gives these devices specific advantages over large-scale reaction systems. For example, resistances that impede the flow of heat and mass are drastically reduced, resulting in great operational agility. Chemical reactions can be rapidly initiated or quenched since thermal response is quick and mixing is essentially instantaneous. In addition, reactions can proceed in modes that are normally unavailable. For example, certain reactions may be conducted under conditions that would normally result in explosion. The ability to rapidly extract heat enables these reaction conditions to be exploited at the microscale. Catalyst materials discovery and development can be carried out efficiently and effectively by the use of microreaction devices. Thin-film deposition methods are well suited to forming diverse multi-component catalyst layers in the composition ranges of interest. Since minuscule quantities of chemicals are used, these systems are very safe from explosion hazard. These small quantities also eliminate risks to the environment. We have designed and fabricated a simple catalytic microreactor for studying heterogeneous reactions and for developing new catalyst materials. Anisotropic wet etching of silicon was used to form devices with microchannel dimensions as small as 5 micrometers. The chip also features backside fluidic interconnects, an anodically bonded glass cover, and sputter deposited catalyst in the reaction zone. We will describe the design, fabrication process, and characterization of the device along with initial reaction results.

SESSION HH6: ENGINEERED ACTIVE SITES

Chairs: Douglas L. Gin and Dick A. Nagaki
Thursday Morning, November 30, 2000
Room 201 (Hynes)

9:45 AM *HH6.1

NOVEL MOLECULAR SIEVE SHIP-IN-A-BOTTLE CATALYSTS. Kenneth J. Balkus, Jr., Godefroy Gbery, Flora Varghese, Sharon Hogue, University of Texas at Dallas, Department of Chemistry, Richardson, TX.

The encapsulation of homogeneous catalysts in zeolite molecular sieve supports has the potential for generating novel hybrid catalysts that combine the advantages of both homogeneous and heterogeneous systems. In this paper, recent advances in the synthesis and characterization of zeolite ship-in-a-bottle complexes will be presented. Examples, of novel systems including the in situ encapsulation of Jacobsen's catalyst in the medium pore MCM-22 during synthesis will be presented. This host/guest system exhibits significantly higher activity in the oxidation of various olefins compared with the homogeneous catalyst. Examples of mesoporous molecular sieve supported catalysts will also be described including glucose oxidase (GOD) immobilized in Ti-SBA-15. In this case, dioxygen was used to form peroxide via GOD, which was then employed by the titanium silicate host to epoxidize various olefins.

10:15 AM *HH6.2

DESIGN, SYNTHESIS AND CHARACTERIZATION OF UNIFORM CATALYST ACTIVE SITES ON SILICA SURFACES. Susannah L. Scott, Dept of Chemistry, Univ of Ottawa, Ottawa, ON, CANADA.

Heterogeneous catalysts typically consist of a multiplicity of active sites of varying reactivity towards substrate. Because catalysis is a surface phenomenon, the designed synthesis of catalytic surfaces through molecular modification permits the construction of arrays of very similar active sites whose kinetic competence in elementary reaction steps of the catalytic cycle can be systematically evaluated. We have examined the ability of simple inorganic and organometallic complexes to generate such arrays through their reactions with hydroxyl-terminated surfaces of various silicas. Metal alkyls, amides, alkoxides and halides generate surprisingly homogeneous (although not always predictable) surface structures with precise and highly reproducible grafting stoichiometries. The combined application of surface spectroscopies, isotope labelling studies and analytical measurements is then implemented to construct an atomic-scale picture of the active site. This approach promises to yield not only more understanding of the catalytic phenomenon, including activation and deactivation processes, but also constitutes a new approach to catalyst discovery and synthesis for high activity and selectivity. Examples relevant to olefin polymerization and selective oxidation will be discussed.

10:45 AM **HH6.3**

THE SYNTHESIS OF MESOCELLULAR SILICEOUS FOAMS AND THEIR APPLICATION TO ASYMMETRIC CATALYSIS THROUGH THE IMMOBILIZATION OF METAL-PHOSPHINE COMPLEXES. John S. Lettow, Dejian Huang, Jackie Y. Ying, Massachusetts Institute of Technology, Department of Chemical Engineering, Cambridge, MA.

The synthesis mechanism of recently developed mesocellular siliceous foams (MCF) has been investigated, and the MCF materials have subsequently been used as supports for novel asymmetric catalysts. The MCF materials are formed by using a microemulsion, consisting of triblock-copolymer micelles whose cores have been swollen by an oil, to template the condensation of tetraethoxysilane (TEOS). After calcination, the synthesis yields silicate materials possessing continuous systems of spherical pores (~30 nm in diameter) connected by "windows" of ~12 nm. Thus, MCF has much larger, more accessible pores than other supermolecular-templated silicates, such as MCM-41, and represents a support much better suited for the catalysis and separation of large, pharmaceutically interesting molecules. The effects of oil concentration and type on the mesostructure of the silicates have been investigated. Furthermore, we have performed small angle neutron scattering (SANS) studies to elucidate the effects of oil type and ethanol content on the micelle structure in the absence of silica. Subsequent studies have followed the structural evolution of the complete reaction mixture. Using these techniques we have been able to deconvolute many of the interactions in this complex system to obtain a better control of the pore size in the novel mesocellular siliceous foams. We will also present the application of the MCF materials to the asymmetric catalysis of hydrogenation reactions. The asymmetric hydrogenation of a prochiral reactant to form an enantiomerically-enriched product is an important step in the synthesis of many single enantiomer drugs. Currently used homogeneous organometallic catalysts are very expensive, not reusable, and can remain as impurities in the products. We have devised a "strong ligand" method for the immobilization of the highly selective homogeneous catalysts onto the surface of the MCF, thus creating a heterogeneous catalyst that can be easily recycled and reused. The enantioselectivity of the MCF hydrogenation catalyst is nearly identical to that of corresponding homogeneous catalyst for a range of reactants. Differences in the activity between heterogeneous and homogeneous catalysts will be discussed.

11:00 AM ***HH6.4**

CHEMICALLY MODIFIED MESOPOROUS MATERIALS AND THEIR USE AS CATALYSTS IN ORGANIC SYNTHESIS. James Clark, Duncan Macquarrie, Karen Wilson, University of York, Clean Technology Centre, York, UNITED KINGDOM.

Increasing public pressure and stricter legislation is forcing the chemical industries to replace inefficient and polluting processes with more environmentally benign chemistry and engineering. The fine and specialty chemicals industries including pharmaceutical manufacturing operate many of their processes at a particularly high waste/product ratio. The processes are typically run in the liquid phase, in batch mode, and often with soluble stoichiometric reagents and volatile organic solvents. The substitution of reagents by catalysts and the use of solid catalysts can substantially reduce process waste through easier separation and catalyst recovery and reuse. Mesoporous inorganic materials such as hexagonal mesoporous silicas (HMS) have suitable pore structures for liquid phase activity for numerous organic reactions. In this paper we will describe the preparation of synthetically useful, chemically modified mesoporous silicas by in-situ (sol-gel) and ex-situ methods. These will include solid Bronsted and Lewis acids, and oxidation catalysts and reagents.

11:30 AM **HH6.5**

HETEROPOLY ACID CATALYSTS SUPPORTED ON MESOPOROUS SILICA. Saemin Choi, Yong Wang, Charles H.F. Peden, Pacific Northwest National Laboratory, Richland, WA.

A lot of industrially important reactions are currently catalyzed by homogeneous acid catalysts. These acid catalysts not only are environmentally hazardous, but also present difficult operations such as waste disposal and product separation. Therefore, solid acid catalysts have been sought in the past decade to replace these problem homogeneous acid catalysts. In this paper, a new class of solid acid catalysts were synthesized based on Cs substituted heteropoly acids and mesoporous silica. The novel procedure of catalyst preparation developed in this research will be disclosed. The unique physical/chemical properties and superior catalytic activities of these newly synthesized solid acid catalysts will be presented.

11:45 AM **HH6.6**

PREPARATION, CHARACTERIZATION AND PERFORMANCE OF A PALLADIUM CATALYST DERIVED FROM A MOLECULAR CLUSTER CARBONYL PRECURSOR IN MESOPOROUS SILICA. Silke Behrens, Eckard Dinjus, Institut für Technische Chemie, Forschungszentrum Karlsruhe, GERMANY.

There is an increasing interest in nano-sized metal particles due to their promising catalytic and electronic properties. With decreasing particle size the ratio of surface to volume increases continuously, so that the particle properties are more influenced by surface atoms instead of lattice atoms. The smaller and the more monodisperse the particles are, the better should be their catalytic activity. The utility of clusters and colloids as precursors for efficient heterogeneous catalysts has already been presented by several groups. We describe the facile deposition of an octanuclear palladium cluster with easily displaceable ligands on MCM-41. The carbonyl cluster Pd₈(CO)₈(PEt₃)₇ is incorporated from solution into the pores of MCM-41 mesoporous silica. By gentle thermolysis of the encapsulated carbonyl metal clusters attached to the surface of the mesoporous silica support finely divided metal nanoparticles are formed. The samples are characterized by X-ray diffraction, N₂-sorption and TEM. These palladium nanoparticles show an interesting reactivity in the catalytic hydrogenation of alkenes. Crotonic acid is tested as standard substrate. The catalysts perform well compared to MCM-41-based catalysts prepared by conventional methods with appropriate palladium salts.

SESSION HH7: CLAYS, METAL HYDROXIDES, OXIDES

Chairs: Levi T. Thompson and George Attard
Thursday Afternoon, November 30, 2000
Room 201 (Hynes)

1:30 PM ***HH7.1**

REHYDRATED HYDROTALCITES AS SOLID BASE CATALYSTS. SYNTHESIS, STRUCTURE AND PERFORMANCE. Krijn P. de Jong, A. Jos van Dillen and Jules C.C.A. Roelofs, Department of Inorganic Chemistry and Catalysis, Utrecht University, THE NETHERLANDS.

Base catalysis plays a major role in fine chemicals manufacture. The drive towards the replacement of liquid-phase base catalysts by solid catalysts has led to significant research activities on hydrotalcites. Hydrotalcites (HT) are a versatile class of anionic clays derived from the brucite structure, Mg(OH)₂, with Al³⁺ replacing part of Mg²⁺ thereby invoking anions needed for charge compensation, to be present in the interlayer spacing. A typical composition is Mg₆Al₂(OH)₁₆CO₃·4H₂O with carbonate anions and water molecules in the interlayer. In 1980 Reichle (Union Carbide) investigated the use of thermally activated (723 K) MgAl-HT as gas-phase aldol-condensation catalyst. Later on, Figueras (IRC, Villeurbanne, 1998) produced highly active MgAl-HT catalysts for liquid-phase aldol condensation by rehydration after thermal treatment. Here we report on a detailed study into the structure-performance relationships of rehydrated HT for liquid-phase catalysis. Mg-Al hydrotalcites have been synthesized by co-precipitation of Mg- and Al-nitrates with sodium carbonate and sodium hydroxide. Using aging at different temperatures (333-473 K) we have obtained HT-platelets over a range of lateral sizes of 0.05 to 0.5 μm. Thermal treatment in nitrogen was studied with a broad array of techniques (XRD, TGA, XAS, TEM, physisorption, CO₂ chemisorption). From a combined use of XRD, XANES, dark-field TEM and physisorption it turns out that thermal activation destroys the layered HT structure to form very small MgO-like domains with micropores being present. Rehydration restores the HT-structure with now Bronsted-base OH-groups as charge compensating anions in the interlayer.

Correlation between catalysis and the structural information strongly supports a new model for the active sites, i.e. catalysis exclusively occurs at interlayer OH-groups present at the edge of the platelets. The catalysts currently obtained display excellent activity (at 273 K) and selectivity in relevant aldol condensation reaction, in particular the self-condensation of acetone to diacetone-alcohol and the condensation of citral and acetone to pseudo-ionones. The latter are important intermediates for fragrances and vitamin-A production.

2:00 PM HH7.2

CATALYTIC ACTIVITY OF ALUMINUM-CONTAINING HETERONUCLEAR HYDROXO COMPLEXES AND CORRESPONDING MIXED OXIDES TOWARDS OXIDATION AND HALOGENATION OF ALKANES. Maximilian Kopylovich, Armando Pombeiro, Centro de Quimica Estrutural, Complexo I, Instituto Superior Tecnico, Lisbon, PORTUGAL.

Many catalytic processes, for example such as oxidation and halogenation of hydrocarbons, Fisher-Tropsch synthesis, reception of synthesis gas etc. could be carried out with use of catalysts on the basis of aluminium oxide. Copper, zinc, nickel, chromium, iron oxides are widely applied as activated components. Such mixed oxide catalysts are received as at coagulating of oxides of separate metals, and at thermal decomposition of the hydroxide mixture. We report now on the application of various aluminum(III)-M(II) hydroxocomplexes and corresponding oxides to the oxidation and halogenation of alkanes. These Al(III)/M(II) complexes were characterized both in solution and in the solid state by potentiometry, dialysis, UV-vis and IR spectroscopy, X-ray phase and thermal analysis. Heterogeneous systems containing oxyhydroxides dispersed in acetonitrile and also homogeneous solutions of hydroxocomplexes were tested towards the halogenation and oxidation by H₂O₂ of e.g. cyclohexane in acetonitrile, and composition-structure-catalytic activity relationships are presented.

2:15 PM HH7.3

NANOSTRUCTURED CATALYSTS OF NO_x SELECTIVE REDUCTION BY HYDROCARBONS BASED UPON ZIRCONIA-PILLARED CLAYS: SYNTHESIS AND PROPERTIES. Vladislav A. Sadykov, V.P. Doronin, T.P. Sorokina, T.G. Kuznetsova, G.M. Alikina, R.V. Bunina, D.I. Kochubei, B.N. Novgorodov, E.A. Paukshits, V.B. Fenelonov, A. Yu. Derevyankin, V.I. Zaikovskii, L.M. Plyasova, A.S. Ivanova, Boreksh Inst. of Catalysis SB RAS, Novosibirsk, RUSSIA; S.A. Beloshapkin, Novosibirsk State Univ, Novosibirsk, RUSSIA; Alexandr Ya Rozovskii, V.F. Tretyakov, T.N. Burdeynaya, M.N. Davydova, Topchiev Inst. of Petrochemical Synthesis RAS, Moscow, RUSSIA; V.A. Matyshak, G.A. Konin, Semenov Inst. of Chemical Physics RAS, Moscow, RUSSIA; J.R.H. Ross, J.P. Breen, Univ. of Limerick, Limerick, IRELAND.

Procedures for synthesis of thermally stable up to 750°C zirconia-pillared clays with specific surface area up to 300-400 m²/g via intercalation of montmorillonite clay with zirconium polyoxocations modified by cations of Ce, Fe, Al, Ca, Sr, Ba were elaborated. A method for correct characterization of the pillared clays structure (the inner arrangement of pillars and pores within crystallites) and texture (a type of crystallites packing into aggregates) is developed and applied for systems under study. This method is based upon analysis of combined XRD and high resolution absorption data in the frames of geometrical model. Optimization of the preparation procedure allowed to obtain samples with the gallery height up to 8 Å, inter-pillar distance being comparable. Clusters of copper and cobalt cations were fixed at pillars using cation exchange, while nanoparticles of Ag and Pt were juxtaposed on them using a photoassisted deposition. The structural and surface properties of pillars and effects of mutual interaction between metal and oxides nanoparticles were elucidated using TEM, EXAFS, SAXS, ESR, TPD/TPR and FTIRS of adsorbed CO/NO molecules. Catalytic properties of these systems were characterized in the reactions of NO_x selective reduction in the excess of oxygen by propane, propylene and decane. Strong interaction between the metal and oxide nanoparticles resulted in substantial variation of the bonding strength and coverages of nitrite-nitrate surface species participating in the rate-determining stage of HC-SCR reactions. It was reflected in substantial improvement of the low-temperature activity and selectivity to molecular nitrogen of these systems as compared with those containing separate components. Catalytic performance of best samples in the NO_x selective reduction by hydrocarbons in the low-temperature (200-300°C) region exceeds that of systems based upon ZSM-5 or traditional alumina supports, while being stable in the presence of water and sulfur dioxide.

SESSION HH8: CARBON AND METAL CARBIDES

Chairs: Levi T. Thompson and George Attard
Thursday Afternoon, November 30, 2000
Room 201 (Hynes)

3:00 PM *HH8.1

SILICON CARBIDE NANOTUBES AND THEIR USE AS CATALYST SUPPORTS. Marc J. Ledoux, Cuong Pham-Huu, Nicolas Keller, Laboratoire de Chimie des Matériaux Catalytiques, ECPM, GMI-IPCMS, CNRS, Université Louis Pasteur, Strasbourg, FRANCE.

Since their discovery at the beginning of the last decade carbon nanotubes have received increasing interest both from the fundamental and the industrial point of view. Carbon nanotubes can exhibit peculiar properties when they are used as catalyst supports. Recently, the synthesis of medium surface area silicon carbide nanotubes with different diameters was achieved in our laboratory. The aim of the present article is to report the preparation and characterization of these materials and their use as catalyst supports for different reactions such as selective oxidation of hydrogen sulfide into elemental sulfur or liquid-phase hydrogenation of cinnamaldehyde. Catalysts supported on silicon carbide nanotubes exhibit a superior catalytic performance for both reactions, compared to those obtained on more conventional catalysts.

3:30 PM HH8.2

NOVEL WATER GAS SHIFT CATALYSTS. Jeremy Patt, Cory Phillips and Levi Thompson, Department of Chemical Engineering, University of Michigan, Ann Arbor, MI .

Recently Mo₂C was demonstrated to be highly active for the water gas shift of a synthetic steam reformer exhaust stream. This catalyst was more active than a commercial Cu-Zn-Al shift catalyst at atmospheric pressure and temperatures between 220 and 295°C. In addition, the Mo₂C catalyst did not deactivate significantly during thermal cycling or extend times on-stream. The incorporation of promoters resulted in substantial improvements in the catalytic activity. The results suggest that high surface area carbides are promising candidates for development as water gas shift catalysts. This presentation will summarize the catalytic properties of selected carbides and describe our present understanding of the mechanism for water gas shift of these materials.

3:45 PM HH8.3

METHANE ACTIVATION ON NANOPOROUS CARBON. Kevin W. McNamara, Henry C. Foley, University of Delaware, Department of Chemical Engineering, Newark, DE.

Methane activation is among the most difficult problems facing chemical scientists and engineers today. The high strength of the methane C-H bond and the saturation of the carbon center render the molecule refractory. Alternative approaches that combine novel chemistry with reaction engineering must be explored to address these challenges. Nanoporous Carbon (NPC) is similar to fullerene soots but is less expensive and its pore structure may be readily manipulated since it is synthesized by the pyrolysis of polymer precursors. Cesium-doped NPC behaves as a solid solution of alkali cations and polyaromatic radical anions. These have been shown to be excellent base catalysts as well as capable of activating other C-H bonds. The methane pyrolysis experiments were carried out a standard packed-bed microreactor. Rigorous precautions were taken to ensure that the highly reactive carbon was kept free from all oxygen contaminants. Comparisons were made between the purely thermal reaction and that catalyzed by NPC and Cs-NPC. Measurable conversion (~1%) was observed with Cs-NPC at temperatures as low as 550C whereas for the purely thermal reaction no reaction is observed until 800C. Interestingly, the NPC alone began to catalyze the pyrolysis at 650°C. Working at 700°C initial conversions of approximately 10% were obtained over the Cs-NPC versus 0% for the thermal reaction and 4.5% over pure NPC. Primary products of this process are ethane, hydrogen and a significant amount of carbon, which deposits on the substrate. More carbon coke and less hydrocarbons are produced over Cs-NPC versus the NPC catalyst. Co-feeding hydrogen with methane inhibited reaction catalyzed by Cs-NPC, supporting the notion that a free radical mechanism is responsible for pyrolysis. The cesium-doped carbon may therefore provide a site for lower temperature free radical initiation to take place.

4:00 PM HH8.4

CHARACTERIZATION OF PLATELET GRAPHITE NANOFIBERS: CHEMISTRY AT THE VERY "EDGE". Paul E. Anderson and N.M. Rodriguez, Northeastern University, Catalytic and Nanostructured Materials Laboratory, Department of Chemistry, Boston, MA.

Platelet Graphite Nanofibers (PGNF) are a new class of novel materials produced from the decomposition of carbon monoxide and hydrogen over iron-based catalysts. The structures consist entirely of edge sites of graphite which gives the material unique electronic properties and great potential as catalyst support media. In this study we have attempted to completely ascertain the 3-dimensional

structural properties through high resolution transmission electron microscopy (TEM). Sonication of the specimens cleaved the structures and revealed cross sections of elongated globular and oblong hexagonal shapes. From electron diffraction analysis and observations of these thin cross sections of fibers, it was possible for the first time to ascertain the amount of {10 $\bar{1}$ 0} (armchair) and {11 $\bar{2}$ 0} (zigzag) faces on the surface. In addition, the fiber surface was probed with temperature programmed desorption/mass spectrometry (TPD/MS) and was found to possess large amounts of oxide species. Upon heat treatment to 2800°C, the structures were transformed from entirely edge sites to entirely basal plane regions. PGNF-supported catalysts maintained activity for longer periods and yielded more nanofiber product when compared to traditional silica supported catalysts. A rationale for this behavior will be presented, which is believed to arise from the electrically conductive properties and geometric effects of the uniquely ordered surface.

4:15 PM HH8.5

NOVEL CARBON SUPPORTED PLATINUM CATALYSTS FOR USE IN ELECTROCHEMICAL DEVICES. Kate Laubernds, Nelly Rodriguez, R.T.K. Baker, Northeastern University, Dept of Chemistry, Boston, MA; Carol Bessel, Villanova University, Dept of Chemistry, Villanova, PA.

The current need for alternative energy sources for automobiles and public transportation vehicles has prompted investigators to focus research efforts on advanced electrocatalysis. One of the most widely researched alternative energy sources is the direct methanol fuel cell. The current drawbacks of this battery that need to be addressed are the high platinum loading and the potential for CO poisoning of the catalyst. We have focused our efforts on the effect of the Pt catalyst support media as well as the effect of adding a second metal, such as Ru, to the Pt host catalyst. Three distinct types of graphite nanofiber supports were compared to the industrial standard, Vulcan carbon. All four support media were characterized by high-resolution transmission electron microscopy and nitrogen BET surface area measurements. The activity towards methanol oxidation and self-poisoning by CO was studied by cyclic voltammetry. Platinum supported on specific types of graphite nanofibers was found to exhibit equivalent activity to that of significantly higher metal loadings on Vulcan carbon. In addition, different behavioral patterns were found with regard to CO poisoning and the performance of the Pt-Ru bimetallic with the four support materials.

4:30 PM HH8.6

CATALYTIC NANOPOROUS CARBON MEMBRANES FOR CONVERSION AND SELECTIVITY ENHANCEMENT. Michael Strano, H.C. Foley, University of Delaware, Dept of Chemical Engineering, Newark, DE.

Catalytic nanoporous membranes, particular those based upon molecular sieving carbon, offer unprecedented opportunities for process intensification through combined reaction and separation. Defect free, nanoporous carbon films of micron scale thickness were synthesized upon macroporous stainless steel supports for use in reactor applications. Ideal gas separation factors for the catalytic membranes were similar to those of inert carbon membranes with He-N₂ = 58.6 and O₂-N₂ = 4.9. One route to high purity isobutylene is through the decomposition of methyl tert butyl ether (MTBE.) Methanol can be reacted with C₄ fractions from refinery off gases to yield MTBE with almost complete selectivity. Subsequent decomposition of the MTBE over an acid catalyst can be used to produce isobutene with few impurities if the reaction takes place at temperatures above about 200°C where selectivity-diminishing side reactions become less favorable. This equilibrium-limited, model reaction system is ideal for benchmarking catalytic membranes in that operation at lower temperatures not only decreases thermodynamic conversion but increases the dominance of unfavorable side reactions - many of which involve the formation of larger molecular weight, bulky products. Nanoporous carbon membranes impregnated with 12-Tungstophosphoric acid have been investigated for use in the selective decomposition of MTBE to methanol and isobutylene. The nanoporous carbon film allows transport of essentially only methanol and isobutylene products and exhibits near total retention of the ether presumably due to its comparatively larger kinetic diameter. The temperature dependence and pressure dependence of the product yield has been shown to be diffusion controlled and modeled using Stefan-Maxwell theory for diffusion through nanoporous solids.

4:45 PM CLOSING REMARKS