

# Nanotechnology in Catalysis

## CATL 33

### **Fabrication of model platinum nanoparticle catalysts by electron beam lithography: Studies of hydrogenation and dehydrogenation of cyclohexene**

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Pt nanoparticle model catalysts with  $28 \pm 2$  nm diameters and  $100 \pm 2$  nm square periodicity have been fabricated with electron beam lithography on silica substrates. The reactivity of the Pt/SiO<sub>2</sub> arrays was compared to a Pt foil for cyclohexene + H<sub>2</sub> at 100° C. The overall reactivity of the Pt particle arrays was higher by a factor of two, the selectivity towards dehydrogenation was three times higher, and the rate of deactivation was about the same as for the Pt foil. Since the primary difference between the nanoparticle array and the Pt foil was the interface between the Pt and the SiO<sub>2</sub>, the interfacial region was most likely responsible for the changes in reactivity on the arrays. Using AFM, SEM, and TPD, the arrays were characterized before and after being exposed to reaction conditions. AFM images of sample cleaned by ion sputtering showed that the pattern of the Pt nanoparticle array was replicated in the silica during the sputtering process. The formation and reactivity of platinum silicide was studied. Hydrogenation rates were higher on platinum silicide as compared to a platinum foil. Platinum films deposited on alumina exhibit the same hydrogenation/dehydrogenation activity as the platinum foil.

## CATL 34

### **Nanostructure processing of advanced catalysts**

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Nanostructured materials are of great interest in catalytic applications. Using supramolecular templating, my laboratory has derived a family of stable mesoporous and microporous transition metal oxide molecular sieves (termed TMS) with well-defined pore structures. The compositional flexibility and pore size tailoring of the TMS system open new possibilities for catalytic applications beyond the silicate-based zeolitic materials or mesoporous MCM-41 structures. The novel nanoporous materials have been used to fixate metalloporphyrins for effective epoxidation and hydroxylation reactions without leaching problems. We have also devised vapor grafting techniques to create highly dispersed Pd coating on nanoporous supports for carbon-carbon coupling reactions, with activities that rival even the best homogeneous Heck catalysts.

## CATL 35

### **New catalytic materials for clean technology**

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The synthesis of many fine and speciality chemicals often rely on homogeneous mineral acids, bases or metal salts, which are frequently used in stoichiometric amounts. Tightening legislation on treatment and disposal of the excessive toxic waste produced on separation and neutralization of the products from this reaction media, is driving industry to consider cleaner technologies, including the use of heterogeneous catalysis. The recent development of templated mesoporous materials, which allow better diffusion of liquid reactants compared to zeolitic materials, has opened up new possibilities for the design of heterogeneous catalysts for use in organic synthesis. Organically functionalized silicas, prepared using these methods, have been designed for use as solid acid, base or even oxidation catalysts. The factors affecting the structure and reactivity of sulphonic acid and amine functionalized silicas will be considered in a range of applications, including esterification and condensation reactions.

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## CATL 36

### Design of open metal sites in porous metal-organic crystals

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A strategy will be outlined for producing open (coordinatively unsaturated) metal sites in porous metal-organic frameworks (MOFs). The PtS net was targeted in the assembly of paddle-wheel type clusters (squares) and adamantane units (tetrahedra).

Copolymerization of 1,3,5,7-adamantane tetracarboxylate (ATC) with Cu(II), under reaction conditions that usually yield the paddle-wheel Cu-C-O structure motif, has resulted in the formation of crystalline Cu<sub>2</sub>(ATC)<sub>6</sub>H<sub>2</sub>O (MOF-11), which adopts a decorated form of the PtS net. Thermal treatment of MOF-11 to remove water guests and ligands, bound axially to Cu(II) centers, yields a porous Cu(ATC) network that is sufficiently rigid to allow its characterization by a single crystal structure. These observations are supported by single crystal structures, gas sorption isotherms, elemental microanalyses, exceptional bond lengths and magnetic coupling constants of the crystals before and after removal of water.

## CATL 37

### Nanofunctionalization of catalysts for methanol-to-olefin chemistry

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We are developing a family of nanostructured catalysts for methanol-to-olefin (MTO) chemistry by ship-in-a-bottle functionalization of the silico-aluminophosphate HSAPO-34. The CHA topology of this catalyst is characterized by nano-cages of 1.0 nm by 0.7 nm diameter that are interconnected through 8-ring windows of ca. 0.38 nm in diameter. We recently reported that catalysts active for the conversion of methanol to olefins require methylbenzene molecules in the nano-cages, and these function as part of the active sites. Ethylene selectivity in MTO catalysis is related to the number of methyl groups on benzene rings trapped in the nanocages. We have developed procedures to either functionalize the methylbenzenes in place or to synthesize other species in the nano-cages, by ship-in-a-bottle routes that modify the catalyst by creating steric constraints in the cages or altering acidity. Catalysts with improved properties have been obtained.

## CATL 38

### Synthesis of nanocrystalline perovskites for catalytic combustion of Methane

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Nanocrystalline perovskites (La<sub>1-x</sub>A<sub>x</sub>Mn<sub>1-x</sub>B<sub>x</sub>O<sub>3</sub>) were synthesized with high surface area and small grain size using chemical co-precipitation. The precipitation conditions were controlled to obtain powders with correct chemical stoichiometry and excellent phase purity. The catalytic activity of these perovskites for methane combustion was investigated for different A and B site substitutions. These novel catalysts allowed for 10% conversion of a stream of 1% CH<sub>4</sub> in air (60,000 h<sup>-1</sup>) at around 350°C, which is comparable to palladium-based catalysts, with full conversion at around 550°C. They are also attractive due to their high thermal and hydrothermal stability. The trends in catalytic activity have been explained by investigating their defect chemistry. Temperature-programmed desorption and coulometric titration were performed to measure the oxygen vacancy concentration and the nature of the surface oxygen species, responsible for activating methane. Increasing the vacancy concentration by appropriate doping at A and B sites was found to enhance activity.

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## CATL 39

### **Nanocrystalline LaCoO<sub>3</sub> based perovskites as catalysts for VOC oxidation**

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A novel perovskites preparation technique involving mechanosynthesis in a high energy ball mill will be reported. This technique allows the formation of nanocrystalline perovskite particles with high specific surface area and high surface defects density.

Typically LaCoO<sub>3</sub> materials are produced with grain size of about 10 nm and specific surface area in the order of 100 m<sup>2</sup>/g when calcined at 200°C. The surface properties

of these materials were investigated by nitrogen BET, temperature programmed desorption of oxygen, XPS (O1s and Co2p photolines), and FTIR of chemisorbed oxygen, CO and NO following calcination at various temperatures. The oxygen storage

capacity was measured by CO oxidation. A comparative kinetic study of four of these LaCoO<sub>3</sub> based materials in the total oxidation of n-hexane and methane was

performed. The rate data are well represented by the following rate equations:

$r = k_1 P_{C_6H_{14}} + k_2 P_{C_6H_{14}}^2$  (1) with  $k_1 = K_1 P_{O_2} / (1 + K_1 P_{O_2})$  (1') and

$r = k_2' P_{CH_4}$  (2) The various rate and equilibrium constants are compared for the four

catalysts, with some of them examined at different temperatures of calcination. The

results are discussed with respect to the nature of the various surface oxygen species involved and the predicted differences in surface defect density.

## CATL 40

### **Recent development in electron microscopy of nanoparticles and supported catalysts**

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Nanoparticles, especially metallic nanoparticles finely dispersed onto high surface-area supports, play an important role in heterogeneous catalysis. The performance of a

supported metal or alloy catalyst can be directly related to the size and spatial

distribution as well as the composition of the metallic nanoparticles. To understand the synthesis-structure-performance relationships of supported catalysts, we need to fully

characterize their structure and, more importantly, their structural evolution during the catalytic reaction. Among many characterization techniques, electron microscopy can

provide structural, chemical, and morphological information on supported catalysts at a nanometer or atomic scale. In this presentation, we will discuss the recent development

in: a) low-voltage imaging and microanalysis of bulk catalyst samples; b) atomic

resolution Z-contrast imaging of nanoclusters; and c) nanoanalysis of individual

nanoparticles by electron energy loss spectroscopy and X-ray energy dispersive

spectroscopy. Applications of these advanced electron microscopy techniques to

characterizing nanoparticles and supported catalysts will be highlighted.

## CATL 41

### **Mixed-metal clusters as precursors for nanoparticle bimetallic catalysts embedded in mesoporous silica MCM-41**

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Improving our understanding of heterogeneous catalysts and applying rationalized

synthetic methods to attain such solids is essential for the development of

environmentally-friendly and economically viable processes. In order to reach both

goals, our strategy is to use well-defined metallic precursors (mixed-metal cluster

compounds), and to disperse them on a well-defined support (the mesoporous silica

MCM-41). A range of bimetallic Cu-Ru, Ag-Ru, Pd-Ru and Sn-Ru cluster compounds has been

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synthesized and characterized. After incorporation inside the channels of MCM-41, they can be thermally activated under mild conditions and yield firmly anchored nanoparticles of known composition, size, and dispersion. These are highly active and selective hydrogenation catalysts, which can be reused without loss of activity. All the materials have been characterized by in situ infra-red and EXAFS spectroscopies, as well as by ex situ high resolution electron microscopy. The shape of the metallic ensembles has been further assessed by theoretical calculations.

## CATL 42

### **Spontaneous formation of gold nanoparticles in MCM-41 mesoporous materials and their application in catalytic hydrogenation of styrene**

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Research on nano-cluster synthesis and their stabilization on various matrices has gained momentum due to their immense importance in catalysis, opto-electronical applications, templates for biominerals, to mention a few. In all the cases the hosts used, either to stabilize the nanoclusters or used as a support, are usually found to be passive and do not participate in the reduction of metal ions to form the metal nanoparticles / clusters. There is hardly any report where the host has been found to participate actively in the reduction of metal ions to form the metal nanoparticles followed by its entrapment in the host matrix. Realizing the immense importance of nano-composites in future applications, we have developed a novel method for the synthesis of gold nanoparticles by spontaneous reduction of aqueous chloroaurate ions (AuCl<sub>4</sub><sup>-</sup>) by MCM-41 type mesoporous molecular sieves as well as by organo-functionalized MCM-41 materials. In this paper the synthesis and characterization of gold nanoparticles obtained by auto-reduction with MCM-41 and organo-functionalized MCM-41 materials is described. The nano-composites obtained by this method are characterized by XRD, UV-Vis, TEM, TGD-DTA analysis and surface area measurements. Catalytic activity shown by this nano-composite in hydrogenation of styrene to ethyl benzene will also be presented.

## CATL 43

### **Transformations of ethylene sulfide on zeolites and a zeotype: The appearance of a seven-membered cyclic product with three ring sulfur atoms on AIMCM-41 - an aluminosilicate with nano size pore system**

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The transformations of ethylene sulfide were studied in a pulse reactor on HY, HZSM-5, and AIMCM-41. The carrier was hydrogen and the reaction temperature was in the range of 423-623 K. As far as the overall reaction is concerned the activity sequence was as follows: HY>AIMCM-41>HZSM-5. Desulfurization, dimerization with the formation of 1,3-dithiolane and 1,4-dithioxane were the main transformation pathways. Most of the sulfur, which was removed during desulfurization, remained attached to the aluminosilicate, however, non-negligible amount either desorbed as hydrogen sulfide (this occurred mainly on HY) or was mopped up in the form trithioxepane (this process took place on AIMCM-41). This latter product is unusual and unexpected and was formed in high concentration only on AIMCM-41. It is not formed on zeolites having either small or medium size pore system. Nano size pores seem to be necessary for this reaction to occur. Interestingly, the straightforward ring opening product, ethanethiol that is, was not observed on any of the materials studied at any temperatures applied.

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## CATL 44

### **Size discrimination of colloidal nanoparticles by thiol-functionalized MCM-41 mesoporous molecular sieves**

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We demonstrate herein that thiol-functionalized MCM-41 mesoporous materials with a well-defined pore size of 40 Å may be used to discriminate between colloidal gold and silver particles in a mixture. More specifically, the thiol-functionalized MCM-41 material selectively entraps colloidal gold particles (size 35 Å) in the pores from a mixture of the gold particles and silver particles of size 70 Å. The gold particles are held in the matrix via thiolate linkage and this process has been studied using UV-vis spectroscopy and thermogravimetry/differential thermal analysis. This approach shows promise for application in bioseparation methodologies as well as in the generation of one-dimensional superstructure assemblies.

## CATL 45

### **Nanoparticles of 3-D transition metal oxides in mesoporous MCM-48 silica host structures: Synthesis and characterization**

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Transition metal oxide nanoparticles were synthesized within mesoporous MCM-48 silica phases. By wet impregnation, drying, and calcination procedures, it was possible to form iron, iron/cobalt, cobalt, nickel, and copper oxide nanoparticles almost exclusively within the pore system. Nitrogen sorption measurements still revealed mesoporosity for the host/guest compounds accompanied by a reduction of the surface area and pore radius, both indications of a decoration/coating of the inner surface of the silica walls. X-ray absorption spectroscopic measurements proved the existence of small, slightly disordered metal oxide nanoparticles. High resolution transmission electron microscopy investigations showed that the mesoporous host structure is still intact after the treatment. Thermogravimetric investigations revealed differences in the reduction/oxidation behavior of the metal oxide nanoparticles compared to their corresponding bulk phases.

## CATL 46

### **Ordered mesoporous carbons exhibiting extraordinary metal dispersion**

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The template synthesis procedure using mesoporous MCM-48, SBA-1 and SBA-15 silicas has been used to obtain ordered mesoporous carbons with various structures such as hexagonal p6m, cubic I4132 and cubic Pm3n. The mesoporous carbons, obtained after the complete removal of the silica template, exhibit the XRD patterns characteristic of regular arrangement of the uniform mesopores (typically 2 ~ 5 nm), narrow mesopore size distributions, high BET specific surface areas and large pore volumes. These ordered mesoporous carbons were able to disperse platinum metals into extraordinary small nanoparticles, compared with the metal impregnation onto other porous carbon supports such as carbon blacks and activated carbons. The nanostructured carbons show great possibilities for applications in new advanced catalyst systems such as fuel cell devices.

## CATL 47

# Nanotechnology in Catalysis

## **Synthesis, characterization, and use of Graphite Nanofibers as novel support materials**

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Graphite Nanofibers (GNF) are a new class of nanostructured carbon materials, synthesized easily from the decomposition of certain carbon containing gases over heated transition metal particles. This talk will give a broad overview of past, current, and future projects involving GNF as a catalyst support, one of many potential applications for the material. Synthetic conditions, which have a direct impact on the nanofiber structure, were found to play a crucial role in the ultimate behavior of GNF as a support. Structural aspects of the nanofiber surface, such as surface anisotropy of graphite basal plane regions and edge faces, on the behavior of supported catalysts will be discussed. Results of current projects, including the use of GNF as supports for methanol oxidation, selective hydrogenation of olefins, and as structural templates for various metal oxide deposition reactions will be presented. The exciting results are accounted for in terms of the availability of the edge regions in GNF, which give the material its interesting conductive and unique structural characteristics. The surface energy associated with GNF materials is not present to the same degree in traditional graphite and nanotube-based materials because of the large exposure of low surface energy basal plane.

## **CATL 48**

### **Mesoporous silica thin films with various structures: In situ time-resolved XRD experiments**

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Highly oriented silica thin films with various structures (2D, 3D hexagonal and cubic) have been produced on silicon and glass substrates by dip-coating technique using cationic surfactant (CTAB) or amphiphilic block copolymers. Their structures have been extensively characterized by combining two-dimensional XRD as well as TEM on film cross-sections. Time-resolved in situ experiments have been used to investigate the formation of such mesostructured films. In the case of CTAB, the organization is extremely fast after film deposition, and involves the formation of intermediate mesophase. For the block-copolymers, the organization is slower, and the interfaces play an important role in the degree of orientation of the micelles. These experiments have been coupled with interferometry experiments to image the film thickness profile and possible mechanisms for the formation of the film mesostructures will be discussed.

## **CATL 49**

### **One-pot synthesis of phenyl-functionalized porous silicates with hexagonal and cubic symmetries**

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The direct reaction of a mixture of phenyltriethoxysilane (PTES) and tetraethoxysilane (TEOS) with an aqueous solution of cetyltrimethylammonium bromide leads to the formation of phenyl-functionalized silicates with cubic Pm3n and 2D p6m symmetries, depending on the experimental conditions (pH, solvent, phenyl content...). Their detailed structural characterization have been performed by means of XRD with synchrotron radiation, one and two-dimensional multinuclear MAS-NMR and adsorption-desorption experiments. The phenyl groups seem to develop specific interactions with the polar head group of CTAB, which stabilizes the formation of the 3D cubic phase. Hydrolytic

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and thermal stability of the samples have been studied, and show a better resistance of the cubic phase with respect to the hexagonal one.

## CATL 50

### **Microwave induced self-assembly of zeolite crystals**

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Nanostructured materials with an organized array have attracted much attention with increasing miniaturization of electronic and mechanical materials. Zeolite is one of the promising candidates for nanoscopically-arrayed materials due to its well-ordered nanoporosity, high surface area and hosting ability for guest species exhibiting new optical, electronic and magnetic properties. Here, we report a noble technique for microwave-assisted fabrication of self-assembled nanoarchitectures such as nanofiber and thin film, which are constructed with zeolite crystals as the building blocks. Metallosilicalite-1 nanofiber (M=Ti, Fe, B, etc.) with MFI zeolite structure can be obtained by self-assembled nano-stacking during the crystallization reaction under microwave irradiation. Metal elements, which are located on the surface of zeolite crystals, seem to act as a nanoglue between the crystals through selective absorption of microwave energy. We can also obtain A-type zeolite thin film on glass substrate via self-assembly of zeolite crystal under microwave irradiation. Microwave effects on preparation of nanostructured materials are also discussed in comparison with conventional hydrothermal heating.

## CATL 51

### **Catalysis by metallic nanoparticles, the good and the bad**

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Metallic nanoparticles have the potential of being excellent catalysts if future applications due to their large surface to volume ratio and the fact that they can be synthesized in colloidal solutions with different shapes. There are new important factors, however, that need to be evaluated before their full potential is utilized e.g. their chemical stability, the fraction of their free surface area, the quality of the surface and the useful temperature range prior to their low temperature surface melting takes place. The good and the bad will be discussed in the talk.

## CATL 52

### **Nanoporous carbon membranes for catalysis and separation**

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Nanoporous carbons (NPC) offer zeolite-like shape selectivities for sharp molecular discrimination without acidity or the creation of a crystalline lattice. Prepared by the pyrolysis of suitable polymer precursors, the materials are characterized by a disordered but regular structure with a pore size distribution narrowly distributed in the vicinity of 0.5 nm. Creation of NPC materials in membrane form is a desirable goal, both from the perspective of exploiting them for real technological applications, but also in order to do better experiments which offer new insights into transport and reaction within their structures. Such highly controlled experiments cannot be done with the material in bulk particle form. We have found that good membranes can be prepared on porous stainless steel by spray coating or ultra-sonically depositing polyfurfuryl alcohol (PFA) resin on them and then pyrolyzing. The resultant materials are robust and are readily converted into a membrane module in either planar or tubular form, from whence experimental data can be derived for single components or mixtures and as a function of

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temperature, pressure, and mole fraction.

The presentation will review at the outset our progress in modeling the intrinsic structure of PFA-derived NPC. Then it will cover the preparation and characterization of planar and tubular modules. Next specific issues will be examined – for example the derivation of membrane thickness from a measure of the transient response to a step function loading of the membrane. New results with catalytic membranes will be described, especially those in which we convert MTBE into its starting components – isobutylene and methanol.

## CATL 54

### **High dispersed nitride supported on $\alpha$ -alumina for hydrogenation of benzene and dehydrogenation of cyclohexane**

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High dispersed nanolevel nitride display outstanding catalytic activities in a variety of reactions, such as ammonia synthesis[1, 2], ethane hydrogenolysis[3,4], ethylene hydrogenation[5,6], hydrodesulphurization[7-9], and hydrodenitrogenation[10-12]. However, only a little attention was paid to its hydrogenation and dehydrogenation for hydrocarbon[13]. The purpose of research described in this paper was to systematically evaluate the hydrogenation of molybdenum nitride supported on  $\alpha$ -Alumina for benzene and dehydrogenation for cyclohexane as well as the effect of secondary element such as Ni and Co.

## CATL 55

### **Performance of nano-nickel particles containing catalyst in the hydrogenation of toluene**

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The paper introduces the physico-chemical properties of a nano-nickel-containing catalyst and its application in hydrogenation of toluene. A comparison test was conducted between the nano-nickel catalyst and a conventional commercial catalyst. The results shows that the activity of the nano-nickel catalyst is much higher than that of the conventional one's.

## CATL 56

### **Cooperative coadsorption of CO and O<sub>2</sub> on gold clusters: Evidence for efficient room-temperature CO<sub>2</sub> generation**

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With the recent discovery of efficient, low-temperature combustion catalyzed by nm-scale supported gold clusters, several groups have reported the size-dependent activity of model gold catalyst systems. This has led to a question of the role of the support material. Using high-pressure flow-reactor techniques, we have studied the adsorption characteristics of selected gold cluster anions with several of the reactants used in the studies of the original supported catalysts: CO and O<sub>2</sub>. Coadsorption experiments have shown the elimination of carbon dioxide from selected clusters. Estimates of turnover frequency indicate that the gas-phase clusters have a catalytic activity of at least 100 times greater than that of the model catalytic systems.

## CATL 57

### **Characterization and catalytic activity of gold nanoparticles synthesized by auto-reduction of**

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## **aqueous chloroaurate ions with fumed silica**

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During the past one decade or so lots of efforts have been directed to understand the physical and chemical properties of different nanoparticles because of their immense importance in catalysis, opto-electronical applications, templates for biominerals, and many more. Importance has also been given to understand the host-guest interaction of organo-inorganic and inorgano-inorganic nano-composite materials. In all the cases the hosts are usually passive and do not participate in the reduction of metal ions to form the metal nanoparticles. Realizing the immense importance of nano-composites in future applications, here we have developed a novel method for the synthesis of gold nanoparticles by spontaneous reduction of aqueous chloroaurate ions ( $\text{AuCl}_4^-$ ) by fumed silica. This is an example of inorgano-inorganic nano-composites where the matrix is actively participating in the reduction as well as support for the nanoparticles. We have also demonstrated the application of this nano-composite in the hydrogenation of styrene.

## **CATL 58**

### **Selective molecular adsorption on gold clusters**

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The adsorption of small molecules (di-oxygen, CO, nitrogen oxides, organic disulfides) on mass-selected gold-cluster anions (4 to 22 atoms) have been investigated, under thermal conditions (high pressures), for their relevance to the low-temperature catalysis by supported gold nanoparticles. Published descriptions of certain of these recent results can be found in: 1) B. E. Salisbury, W. T. Wallace, R. L. Whetten, Low-temperature activation of molecular oxygen by gold clusters: A stoichiometric process correlated to electron affinity, *Chem. Phys.* 262 (2000) 131-141. 2) W. T. Wallace, R. L. Whetten, Carbon monoxide adsorption on selected gold clusters: Highly size-dependent activity and saturation compositions, *J. Phys. Chem. B* 104 (47)(2000) 10964-10968.

## **CATL 59**

### **Size-dependent electrical behavior of spatially inhomogeneous barrier height regions on silicon**

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A series of ordered, periodic arrays of low barrier height n-Si/Ni nanometer-scale contacts interspersed among high barrier height n-Si/liquid contacts has been prepared by evaporating Ni through bilayers of close-packed latex spheres deposited on n-Si. By varying the diameter of the spheres from 174 nm to 1530 nm, geometrically self-similar Si/Ni structures were produced having triangular Si/Ni features ranging from approximately 100 to 800 nm on a side. The resulting Si surfaces were used as electrodes in methanolic electrochemical cells containing  $\text{LiClO}_4$  and 1,1'-dimethylferrocene+/o. The current density-voltage and photoresponse properties of the resulting mixed barrier height contacts were strongly dependent on the size of the low barrier height contact regions even though the fraction of the Si surface covered by Ni remained constant. These observations are in excellent agreement with the behavior predicted theoretically by the "pinch-off" effect. The current-transport properties of these Ni-patterned electrodes suggest that the effective barrier height experienced by majority carriers approaching the nanopatterned contacts is higher than the barrier height of a uniform Si/Ni contact. These nanopatterned structures may be useful in catalysis as

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well as in interfacial electron transfer processes.

## CATL 60

### **Tin-indium oxide nanocomposites for gas sensor applications**

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Conventional gas sensors are limited by several characteristics. First, gas sensors tend to have poor long-term stability and response reproducibility from one device to the next. Secondly, the selectivity for various gases that come in contact with the sensor is poor. Current sensors also suffer in response time.

In our research, novel tin oxide-indium oxide (SnO<sub>2</sub>-In<sub>2</sub>O<sub>3</sub>) semiconductor nanocomposites have been designed and synthesized via wet-chemical approaches. They display superb thermal stability and sensitivity to ppm levels of CO and NO<sub>x</sub>. By controlling the SnO<sub>2</sub>-In<sub>2</sub>O<sub>3</sub> microstructure and composition, and by introducing active dopants, sensors with excellent selectivity for CO and NO<sub>x</sub> have been successfully attained and optimized.

## CATL 61

### **Catalytic Properties of Mixed Nanoparticles**

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A series of mixed metal oxide catalysts, in which the catalysts are formed from a designed mixture of nano-sized alumina, silica, and titania, has been prepared. Surface area measurements and pore size distributions for the materials have been determined. A series of probe reactions and chemisorption experiments have been used to examine the relative reactivities and adsorption site densities of the different materials. In situ diffuse reflectance infrared spectroscopy has been used to examine the surface reactions, while microreactor experiments have been used to investigate the kinetics and product yield of the different materials for the probe reactions. TGA measurements carried out at a variety of temperatures have been used to determine adsorption isotherms for the mixed nanocatalysts. The results of these characterization probes as a function of composition for the mixed nanocatalysts will be presented.

## CATL 62

### **Preparation and Characterization of Sulfated Zirconia/Silica Super Acid Nano-catalyst**

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Nano-dispersed sulfated ZrO<sub>2</sub>/SiO<sub>2</sub> super acid catalysts have been prepared by sol-gel technique. In there, the silica precursor tetraethyl orthosilicate was hydrolyzed under HCl-catalysis, while zirconium butoxide was hydrolyzed to colloidal particles with diameter of 0.72 nm in the presence of a large amount of sulfate for the construction of solid super acid. After the two transparent sols were homogeneously admixed at various ratios (Zr/Si=30, 40, 45, and 50 mol%), a certain amount of cross-linking agent was added into the system to prevent ZrO<sub>2</sub> colloids from self-aggregating. The obtained gels were sintered in N<sub>2</sub> at 550°C to the ZrO<sub>2</sub>/SiO<sub>2</sub>-catalysts desired. The properties of the catalysts were characterized by TPD-NH<sub>3</sub>, X-ray, and XPS. The results indicate that the acid strength of the amorphous ZrO<sub>2</sub>/SiO<sub>2</sub>-catalyst of 40mol% exhibits the strongest and a rather sharp distribution at 530°C -580°C due to the formation of sulfated zirconia on silica surface.

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## CATL 63

### **Highly selective dehydration of 4-methyl-2-pentanol to terminal olefin catalyzed by (hydrous) zirconia solid catalysts**

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Much work has been done on the dehydration of alcohols on oxide catalysts, with much attention devoted to alumina. By using this oxide, the dehydration of alkan-2-ols mainly resulted in alk-2-enes. Although high alk-1-ene selectivity has been reported by using the oxides of some elements from group 3, 4, and 13, there left a lot to be desired as to the selectivity to the alk-1-ene [1]. (Hydrous) zirconia is a kind of typical and important acid-base bi-functional solid catalyst. It has been investigated in a series of important reactions [2]. Since the acid-base properties of solids are involved in the catalysis of alcohol dehydration reactions, it is very interesting to investigate zirconia in the dehydration of 4-methyl-2-pentanol, which leads to the production of 4-methylpent-1-ene [3]. Recently, the preparation of high-surface-area (hydrous) zirconia was investigated extensively in our lab. And to extend this research into the catalytic reaction studies, we applied our high-surface-area (hydrous) zirconia into a series of alkan-2-ols dehydration reaction, including 4-methyl-2-pentanol, 1-cyclohexylethanol and 2-cyclohexylethanol. Before being used in the dehydration reactions, different batches of (hydrous) zirconia catalyst were subject to different alkali-metal ion treatment. Dehydration experiments were carried out at a fixed catalyst bed/vapor-phase reaction system at atmospheric pressure. Usually, the vapor of feed alcohol is diluted with helium before passing through the catalyst bed. Preliminary experiment results showed that (hydrous) zirconia with proper treatment were highly selective towards the production of 1-alk-1-ene. In some cases, as high as 90% conversion of 4-methyl-2-pentanol and 85% selectivity to the desired alk-1-ene can be achieved at certain reaction temperature and flow rate of carrier gas. The effect of content of alkali-metal ion and flow rate of carrier gas have been investigated to obtain the optimal dehydration reaction conditions as to achieving high selectivity to alk-1-ene at rather high conversion of alcohol reactants. In conclusion, when properly adjusting the acid-base properties of (hydrous) zirconia catalyst, it is possible to achieve high selectivity to alk-1-ene at high conversion of alcohol, which led to high yield of the desired alk-1-ene product.

## CATL 64

### **Synthesis of Ti-MWW as a catalyst for selective epoxidation of alkenes**

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We have succeeded in the synthesis of Ti-MWW for the first time by using boron (III) as crystallization enhancing cations. Ti-MWW was hydrothermally synthesized under alkali-free conditions with the coexistence of boric acid and using piperidine as a structure-directing agent. The as-synthesized Ti-MWW precursor samples having layered structures with Si/Ti ratios of 20-100 were refluxed with acid solution to extract the extraframework Ti species together with most of framework boron. Acid washing after calcination gave rise to poor catalysts because of the formation of the anatase phase. Ti-MWW was active for the epoxidation of alkenes and functionalized alkenes. Ti-MWW obviously exhibited activity and product selectivity superior to TS-1. The use of hexaethyleneimine as a structure-directing agent produced less active catalyst, which was ascribed to the difference in the crystal size and morphology between the two catalysts.

## CATL 65

### **Construction of multisite chiral catalysts: Dendrimer-fixation of C<sub>2</sub>-symmetrical diphosphinerhodium complexes**

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Dendrimers, due to their high symmetry and rigid structures, are currently more and more examined as interesting nano-size supports for novel catalytic phases. In the course of our work on the fixation of different organometallic and coordination compounds on dendrimers, we synthesized polypropyleneimine-dendrimers bearing

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specially functionalised derivatives of C2-chiral phosphines and their rhodium(I) complexes. This paper will present our synthetic strategies as well as first results of applications in catalysis obtained with these new, multisite-functionalised compounds.

## CATL 69

### **Design activity and selectivity in tailored nanoscale materials**

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This presentation will discuss synthesis of tailored nanostructured materials, and novel strategies to control the activity and selectivity of such materials. The development of microporous and nanoporous materials based on a molecular templated approach opens new opportunities for catalyst synthesis. For example, the introduction of self-assembled functional molecules in the porous hosts makes it possible to systematically change the surface property and the activity of the materials. This approach not only produces simple acid and base catalysts that utilizes one kind of active group, it can be also used to synthesize multifunctionalized nanoporous materials in which the catalytic activity depends on properly spaced multifunctional groups. In addition, using a molecular imprinting techniques, hierarchical porous materials can be synthesized that contain rigid nanoporous oxide frames, coated by soft, "microporous" molecular monolayers. The size and the shape of the cavities embedded in the long-chain molecular monolayers determine the size-and-shape selectivity of the new material. By properly choosing the template molecules, the size and shape of the cavities can be systematically varied. Furthermore, we can take advantage of the conformational changes of the long-chain molecules in the monolayer to regulate the accessibility of the microporous cavities in the monolayer, a property usually observed in biomembranes, but not in inorganic microporous materials. Similar molecular assembly approaches can be extended to microporous zeolites, using supercritical fluid as the delivery media for the functional molecules. Functionalized microporous acid catalysts have been developed, which demonstrated good size and shape selectivity. \*This research is supported by the Office of Basic Energy Sciences, Materials Division, of the Department of Energy.

## CATL 70

### **First principles simulations of catalysis and nanotechnology**

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We report first principles simulations (quantum mechanics and molecular dynamics) to describe the catalytic mechanism for forming nanoscale systems (such as single wall nanotubes) and to model the chemical reactions in nanocatalysis

## CATL 71

### **Amphoterization and Layer-by-Layer assembly of Colloidal Gold Particles Deivatized with the Amino Acid, Valine**

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The surface modification of colloidal gold particles with the amino acid, valine, is demonstrated. Self-assembly of valine on the gold particles is accomplished in the aqueous phase, linkage with the gold particles possibly occurring through covalent interaction of the amine group with the surface gold atoms. Derivatization with the amino acid in this manner imparts amphotericity to the gold particles, the particles being negatively charged at pH values greater than 6 and positively charged below this pH. The charge reversal on the gold particles is demonstrated by electrostatic self-assembly

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of the colloidal gold particles on glass by immersion of the substrate alternatively into the valine-capped gold solutions maintained at pH=3.5 and 8.5. The stability of the valine-capped gold colloidal solution at these pH values has been studied using UV-vis spectroscopy while the superlattice structures on glass have been characterized by UV-vis spectroscopy and X-ray photoemission spectroscopy.

## CATL 72

### **Autocatalytic formation of nanometer-sized metal particles during photographic development and in colloidal dispersions**

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Self-accelerated generation of Ag crystallites is a key step for producing images during photographic development, where Ag clusters produced by light aid silver amplification. A simple autocatalytic model was found that can rationalize all the available kinetic data of both direct and physical development. In this mechanism the Ag clusters grow until they form nanoparticles which can establish an ohmic contact with the AgBr semiconductor. After completion of the growth step, electrons from the metal delocalize into AgBr and reduce silver ions. Autocatalysis arises from increases in the number of the Ag particles, not due to increases in particle size. Autocatalytic rate laws are also consistent with kinetic data from the formation of Au and Pt colloids with the popular citrate synthesis. For these systems the proposed mechanism involves diffusion of radical reductants away from the metal surface into the solution, where they initiate further formation of particles.

## CATL 73

### **EXAFS investigation of bimetallic materials for the synthesis of single-walled carbon nanotubes**

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Extend X-ray absorption fine structure (EXAFS) has been used to investigate Ni/Co catalytic materials collected from a laser synthetic apparatus making single-walled carbon nanotubes. Based on the EXAFS results of the coordination number of the nearest neighbors, we conclude that Ni atoms are more likely to be found at or near the surface of these materials. Co in the materials, on the other hand, resembles closely to that in the bulk. We have also investigated other types of metal nanoparticles using EXAFS. The results will be presented.

## CATL 74

### **Preparation and characterization of catalyst applied for synthesis of carbon nanotubes via CCVD method**

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Alumina supported Co, Fe and Co-Fe catalysts were prepared by impregnation of alumina with 0.1 M aqueous solution of the respective nitrate salts and were characterized by physico-chemical techniques including the test of their efficiency in production of carbon nanotubes from acetylene at 1000 K. TEM and SEM images showed that no tube formation took place on Fe/alumina and a small amount of carbon nanotubes were found on Co/alumina samples. On these samples the generation of thin carbon fibers was predominant. However, the bimetallic Co-Fe/alumina sample produced carbon nanotubes very effectively. On this sample well-graphitized multiwall carbon nanotubes with an outer diameter of 8-12 nm were detected by TEM. The average length/diameter ratio of the tubes determined from TEM images was around 800-1000. To explain of these experimental observations XPS measurements were

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performed. The results showed that a bimetallic alloy phase generation could be assumed that formed upon heat treatment of catalysts samples in reductive hydrocarbon atmosphere. The different performance of the catalysts tested is traced back to the carbide and acetylide forming capability of the catalysts.

## CATL 75

### **Degradation of organic contaminants in drinking water and wastewater using a rotating disk photocatalytic reactor: Factors affecting interfacial transport, adsorption, and reaction**

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This study investigates the effect of interfacial mass transport of reactant solutes from the liquid and gas phases to the semiconductor solid phase, their adsorption at the nanoscale TiO<sub>2</sub> semiconductor surface, and their reaction with the photo-generated charged carrier species. In this complex three-phase process of the Rotating Disk Photocatalytic Reactor, each of these mechanisms becomes important under certain regimes. Unveiling these regimes by proper selection of process operational and experimental conditions results in determination of the extend of contribution by each regime to the overall photocatalytic degradation process. As a result, the intrinsic reaction kinetics can be determined under conditions in a regime which is not influenced by mass transfer. Combining information from adsorption equilibrium studies and photocatalytic studies, it is possible to select the appropriate reaction model that describes the overall degradation kinetics.

## CATL 76

### **Simulation of the dynamic behavior of nanoparticle chain aggregates**

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Previous electron microscope studies in our laboratory have shown that nanoparticle chain aggregates (NCA) of inorganic oxides have elastic properties. Measurements were made with titania, alumina, and iron oxide NCA generated by laser ablation. Primary particles were 5 to 10 nm in diameter, and mobility diameters of the NCA studied were of the order of 0.5 microns. NCA stretching appears to begin with the rotation and/or sliding of adjacent nanocrystals. Most of the NCA lengthening results from the separation of kinked chain segments held together by weak, probably van der Waals forces. NCA strains up to 90% were observed. The current study compares the experimental results with those obtained by constrained molecular dynamics applied to model systems of nanoparticle chains. The potential function we are using in our model is based on the van der Waals interaction among the primary particles. We explore case studies, where only certain fragments of the chain are allowed to rotate and/or slide relatively to each other. The dynamic behavior of chain aggregates may have applications to the properties of composite materials that incorporate NCA, such as commercial rubber, and to the biological effects of inhaled NCA such as diesel soot.