

9-01

Methanol Oxidation to Methyl Formate and Dimethoxymethane on Supported RuO_x and H₃PV_xMo_{12-x}O₄₀ Clusters

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RuO_x and H₃PV_xMo_{12-x}O₄₀ clusters catalyze CH₃OH oxidation to methyl formate (MF) and dimethoxymethane (DMM) at near ambient temperatures. DMM synthesis involve bifunctional redox-acid pathways favored by acidic supports. The concurrent formation of dimethylether can be inhibited by titration of acid sites with organic bases to form stable pyridine-polyoxometallate (POM) composite catalysts with high DMM selectivity. Reaction pathways involve catalytic redox cycles using lattice oxygen atoms on active oxides to form primary formaldehyde products and secondary reactions of methoxymethanol or hemiacetal intermediates to form MF on supports containing dehydrogenation functions (ZrO₂, SnO₂) and DMM on acidic supports (Al₂O₃, SiO₂). Kinetic and isotopic studies showed that initial HCHO synthesis is limited by C-H bond activation on lattice oxygens on both RuO_x and POM clusters.

9-02

Chemistry-Aided Design of Future Clean Fuels

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Clean fuels are the result of a continuum of changes in the chemical composition of gasoline and diesel. The removal of lead from gasoline in the 1970s, the addition of oxygenates in the 1990s, and the current removal of sulfur each impacted the chemical composition of fuels. Understanding the interaction between fuel composition and process chemistry enables not only optimal application of current refining processes but also development of new approaches to produce clean fuels. For example, utilizing detailed analyses of the distribution of sulfur-containing molecules in refinery streams, reactor models are now used to both design new hydrodesulfurization units and integrate them with existing units. Similarly, molecular analyses of gasoline streams suggest methods to minimize octane loss during the production of ultra-low sulfur gasoline. These and other examples will be used to discuss the impact of future clean fuel requirements on fuel composition and processing.

9-03

The Role of Liquid Products in Catalyst Pores for Influencing Product Olefin Readsorption and Hydrocarbon Chain Initiation in Fischer-Tropsch Synthesis

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During Fischer-Tropsch synthesis, catalyst pores are filled with waxy liquid product hydrocarbons. This liquid phase helps to increase the overall reaction rates for the readsorption of product α -olefins which in turn increase hydrocarbon chain initiation. This results in non-linear Flory product distribution and the formation of a heavier more paraffinic product slate. We use transition state theory to show that higher olefin readsorption rates of larger olefins are not the result of higher solubility of olefins in the liquid phase. Increasing olefin solubility is

either unimportant for olefin readsorption, or, under certain circumstances, would actually increase the tendency of adsorbed olefins to desorb rather than of solvated olefins to readsorb. Thus the olefin solubility – physisorption model is inconsistent with transition state theory and with experimental observations. Instead, the liquid hydrocarbon phase within catalyst pores introduces an intraparticle transport limitation on the olefin products as they exit these pores. These intraparticle diffusion limitations induce fugacity gradients that lead to the observed enhanced olefin adsorption as olefin size increases within catalyst pores.

9-04

C-H Bond Activation by Platinum

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C-H bond activation for several alkenes (ethylene, propylene, isobutene, cyclohexene, and 1-hexene) and alkanes (methane, ethane, n-hexane, 2-methylpentane, and 3-methylpentane) has been studied on the (111) crystal face of platinum as a function of temperature at low (< 10⁻⁶ Torr) and high (1 Torr) pressures in the absence and presence of hydrogen pressures (10 Torr). Sum frequency generation (SFG) vibrational spectroscopy has been used to characterize the adsorbate structures and high pressure scanning tunneling microscopy (HP-STM) has been used to monitor their surface mobility under reaction conditions during hydrogenation, dehydrogenation, and CO poisoning. C-H bond dissociation occurs at low temperatures ~250 K, for all of these molecules, although only at high pressures for the weakly bound alkanes because of their low desorption temperatures. Bond dissociation is known to be surface structure sensitive and we find that it is also accompanied by the restructuring of the metal surface. The presence of hydrogen slows down dehydrogenation and for some of the molecules it influences the molecular rearrangement, thus altering reaction selectivity. Surface mobility of adsorbates is essential to produce catalytic activity. When surface diffusion is inhibited by CO adsorption, ordered surface structures form and the reaction is poisoned. Ethylene hydrogenation is surface structure insensitive, while cyclohexene hydrogenation/dehydrogenation are structure sensitive. n-Hexane and other C₆ alkanes form either upright or flat lying molecules on the platinum surface that react to produce branched isomers or benzene, respectively.

9-05

Parameter Estimation in Nonlinear Models when the Estimates Really Matter

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Classical Nonlinear Design of Experiments and Analysis Strategies are available for discriminating rival kinetic models for catalytic reaction systems and for generating minimum variance parameter estimates for the model selected. These methods are rarely used because of the lack of understanding of their statistical underpinnings by the modeling community, the convenience of linear statistical methods and companion hostility of nonlinear estimation procedures, and finally, the lack of importance of high quality parameter estimates. The ushering in of the era of design informatics has changed this paradigm. It is now critical to estimate high quality microkinetic rate constants and use them as response variables to characterize other

physiochemical properties of the catalyst. The power and storage capabilities of the high speed computers are now making it possible to realize design and analysis capabilities which permit the relaxing of questionable assumptions in classical methods while simultaneously providing a more user friendly environment. In this talk we will define and illustrate the need and consequence of applying Markov Chain/MonteCarlo procedures to Bayesian estimation to generate high quality parameter for a simple reaction system. A novel adaptive gridding technique developed to address the computation challenges will also be presented. Finally, generalization of the procedures introduced to more complex system will be discussed.

9-06

Mobility of Catalytic Nanoparticles

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Sintering of catalysts is an important mechanism for catalyst deactivation. The active phase in these catalysts consists of nanosized metal particles, which can transform at elevated temperatures into particles as large as few hundreds of nanometers leading to loss of activity and selectivity. One of the proposed mechanisms involves the migration and coalescence of nanoparticles. Models for catalyst sintering assume that the diffusion of nanoparticles on surfaces scales with (particle diameter)ⁿ, where the exponent n can vary from -4 to -7. Such models imply that as particles grow in size, the rates of migration and coalescence will slow down. In this work, we will report systematic studies of the migration of nanoparticles on oxide surfaces at sizes ranging from a few atoms to several tens of nanometers. We have used a variety of techniques, ranging from scanning tunneling microscopy, scanning electron microscopy as well as transmission electron microscopy. We also performed Monte Carlo simulations of nanoparticle dynamics. The results provide many surprises and show that the phenomenon of nanoparticle mobility is very complex and involves several competing mechanisms.

9-07

Scanning Transmission Electron Tomography and Supported Nanoparticle Catalysts

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It is desirable to develop non-destructive methods of determining the distribution of sub-nanometer metallic and bimetallic catalysts supported on highly porous oxides. In particular, the location of nanoparticle Pt-Ru catalysts, which exhibit high activities and selectivities in the hydrogenation of polyenes and other organic compounds, needs to be precisely determined when the siliceous support is composed of non-ordered nanopores of average diameter ca 6 nm. The advantage of doing so using dark-field (rather than bright-field) annular scanning electron microscopy, which can also be adapted to retrieve the elemental composition of individual particles weighing as little as a few zeptograms (10^{-21} g), will be outlined.

9-08

A New Approach to Obtain Highly-Dispersed Supported Ru/SiO₂ Catalysts

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Preparation of metal catalysts is an old field with few new directions discussed in either the academic or patent literature. Most supported metal catalysts are prepared from the corresponding supported metal oxides, classically by incipient wetness impregnation of solutions containing metal salts, followed by drying and then calcination to form the oxides. By changing the preparation method, the interaction between the supported oxide and the support changes, which in turn modifies reducibility and dispersion of the supported metal. Here we report a new approach specifically for preparing well-dispersed supported Ru catalysts on silica. We show that partially oxidizing a Ru- triethanolamine impregnate on silica forms a strongly interacting precursor, which bonds to and spreads on the support. This precursor avoids the necessity of using rigorous anaerobic conditions or esoteric precursors to form supported organometallic complexes. Reduction of this Ru-precursor creates tiny metal crystallites homogeneously distributed on silica, in sharp contrast to what occurs via traditional impregnation routes. This homogeneous distribution also leads to enhanced resistance to reductive sintering, which we clearly demonstrate by chemisorption and TEM techniques. We present preparation, characterization and aromatic hydrogenation data to illustrate this new technique of preparing supported Ru catalysts.

9-09

Poisoning and Deactivation of Cobalt-based Fischer-Tropsch Catalysts By ppm And Sub-ppm Level Reactive Nitrogen Compounds

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Sulfur poisoning of cobalt Fischer-Tropsch catalysts has been known since the earliest days of the technology, and is the subject of numerous scientific publications, including a number by Prof. Bartholomew in the 1980s. More recently extensive work has been conducted in the area of cobalt FT catalyst deactivation due to surface oxidation and/or spinel formation due to high water concentrations and/or water-to-hydrogen ratios. Part per million levels of reactive nitrogen compounds – mainly ammonia, with smaller amounts of hydrogen cyanide and possibly nitrogen oxides – are typically formed in synthesis gas generation processes. The patent literature contains numerous claims for the need, and methods, to remove these compounds from FT synthesis gas feeds but to date very little/no published information exists regarding the actual details of nitrogen compound induced poisoning/deactivation.

We have investigated the effects of NH₃, HCN, and NO_x both when added to laboratory fixed bed and slurry autoclave synthesis gas feeds and when present in real autothermal reformer/catalytic partial oxidation synthesis gas in a pilot plant scale slurry bubble column reactor. The results of these studies indicate markedly different effects from nitrogen than from sulfur or water induced deactivation mechanisms. The presence of reactive nitrogen compounds initially causes a rapid, though limited, loss of activity. In this regime the deactivation rate is directly proportional to the nitrogen compound feed space velocity. During this phase, the

number of impacted sites appears larger than the number of nitrogen atoms involved, but is limited to suppressing activity by only about 35%. Continued operation yields much lower further deactivation rates that are only weakly dependent on the nitrogen compound concentration and space velocity. Nitrogen poisoned catalysts operated with clean synthesis gas feeds show a very slow reactivation, but essentially 100% activity can be easily restored through a relatively mild in-situ hydrogen treatment.

9-10

Spectroscopic Identification of Carbonaceous Species on Silica-Supported, and Platinum-Promoted Iron Fischer-Tropsch Catalysts

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Carbonaceous surface species and bulk iron carbides formed under commercially-relevant Fischer-Tropsch synthesis (FTS) conditions on moderately dispersed, high-activity silica-supported iron catalysts (Fe/SiO_2 , FePt/SiO_2 and $\text{FePtK}/\text{SiO}_2$) were spectroscopically characterized. Bulk iron phase compositions were determined by Mössbauer spectroscopy, and phase transformations of carbonaceous species during pretreatment with CO , H_2 , or H_2/CO and following reaction were characterized using temperature-programmed hydrogenation (TPH). Isothermal transient rates of FTS were also measured for catalysts after different pretreatments.

Six surface and bulk carbonaceous species were quantitatively identified from combined TPH and high-pressure Mössbauer spectra of the FePtK catalyst; They include, in order of decreasing reactivity: (a) adsorbed, atomic carbon (C_γ); (b) amorphous, lightly poly-merized hydrocarbon or carbon surface species (C_γ); (c) bulk γ and δ carbides ($\text{Fe}_{2,2}\text{C}$ and $\text{Fe}_{2,5}\text{C}$); and (d) disordered and moderately-ordered graphitic surface carbons. The distribution of active and inactive carbon species varies with pretreatment and time-on-stream. A correlation between the amount of reactive α -carbon (C_a) and initial catalytic activity after different pretreatments was observed. The method of Li et al.¹ for determining irreversible chemisorption of CO does not measure active site densities on silica-supported iron quantitatively. Nevertheless, specific activity based on H_2 chemisorption after reaction may be proportional to active site density. Models, based on this and previous work, are proposed for iron phase and carbon phase transformations in silica-supported iron during pretreatment, FTS, and post-reaction passivation/oxidation.

9-11

Structure-function Relationships in Pd-Au Catalysts

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Model mixed-metal catalysts consisting of Pd alloyed with Au as bulk films on refractory metal single crystals and as nanoparticles supported on oxides have been characterized using an array of surface techniques including X-ray photoemission spectroscopy (XPS), low energy ion scattering spectroscopy (LEIS), Auger electron spectroscopy (AES), low energy electron diffraction (LEED), infrared reflection absorption spectroscopy (IRAS), metastable impact

electron spectroscopy (MIES), scanning tunneling microscopy (STM), temperature programmed desorption (TPD), and reaction kinetics. The surface sensitivity of LEIS and IRAS has been exploited for elucidating atomic composition of the outermost surface layer. Of special interest is the composition of the surface compared to the overall composition, particularly in transitioning from planar surfaces to nanoparticles, in the presence and absence of adsorbates. The mechanistic details of the vinyl acetate synthesis reaction, used to probe the structure-function relationship of these alloy surfaces, will also be discussed.

9-12

The Nature of the Active Sites in Au/TS-1 Catalysts for Propene Epoxidation by Oxygen and Hydrogen

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Partial oxidation of propylene to propylene oxide (PO) by $H_2 + O_2$ over Au/TS-1 as a function of TS-1 particle size showed the number of active sites to be limited and that reaction may occur within the TS-1 crystallites. Catalysts prepared with low titanium and low gold loadings confirmed the presence of a small number of very active Au/Ti sites, formed more efficiently at low loadings. A catalyst consisting of 0.01 wt % Au on TS-1 with a Si/Ti = 500 was found to have the highest activity per gold atom yet reported ($350 \text{ g}_{PO} \text{ hr}^{-1} \text{ g}_{Au}^{-1}$ at 200°C). These catalysts were also shown to have an inherent gold uptake that, when exceeded, produced inferior PO rates and stability. Density functional theory (DFT) results showed that hydrogen peroxide could be produced catalytically from oxygen and hydrogen over gas phase Au_3 , Au_4^+ , and Au_5^- , favored in that order. TS-1 synthesized in the presence of carbon pearls gave the highest activity per gram catalyst ($132 \text{ g}_{PO} \text{ hr}^{-1} \text{ kg}_{cat}^{-1}$: 0.33 wt % Au on TS-1 with a Si/Ti = 28, 200°C). We conclude that H_2O_2 is the oxidant and that small clusters of Au atoms near Ti are viable sites for PO production.

9-13

Poisoning, and Fouling of V_2O_5/TiO_2 SCR Catalysts by Ash from Coal- and Biomass-Fired Boilers

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A comprehensive study of deactivation of V_2O_5/TiO_2 SCR catalysts by ash minerals from coal- and biomass-fired boilers was undertaken at laboratory and small pilot plant scales. Laboratory activity tests to determine effects of poisoning by basic ash components were conducted on commercially-relevant 1% $V_2O_5/9\% \text{ WO}_3/TiO_2$ catalysts pre-impregnated with various levels of soluble Na and Ca compounds. These experiments simulate possible poisoning of "dusted" SCR catalysts during exposure to flue gas below the dew point. Significant losses of activity with increasing Na or Ca concentrations are observed, although at Na/V and Ca/V ratios greater than one, activity level approaches a constant low value which is nevertheless still measurable. Loss of activity is significantly greater for Na relative to Ca compounds. These results suggest that substantial loss of activity is associated with adsorption of basic cations on the acid sites of V_2O_5/TiO_2 , although poisoning of sites is not complete at saturation coverage by the poison.

Surface sulfation by SO₂ of 1-5% V₂O₅/TiO₂ catalysts during reaction, on the other hand, increases catalytic activity. *In situ* FTIR spectroscopy and XPS analyses indicate that SO₂ is not adsorbed as a sulfite or sulfate on vanadia sites but rather on titania sites. Sulfation by SO₂ also enhances NH₃ adsorption on Brønsted acid site but not on Lewis acid sites; this suggests that sulfation may occur on sites at the interface of vanadia surface species and TiO₂. NO reduction activity of both fresh and sulfated vanadia catalysts increases due to an increase in the number of active sites without changing activation energy.

Five commercial vanadia-based catalysts and a monolith catalyst prepared at BYU were tested over several thousand hours in a small pilot plant reactor using slipstreams from commercial boilers in which coal and biomass-coal blends served as fuels. Post mortem, laboratory activity studies of the monolith catalysts after various exposure times indicate that fouling and plugging rather than poisoning are the main deactivation mechanisms for vanadia catalysts under commercial operation.

9-14

Renewable Liquid Alkanes from Aqueous-Phase Processing of Biomass-Derived Carbohydrates

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Concerns about global warming, national security and the diminishing supply of fossil fuels are causing our society to search for new renewable sources of transportation fuels. Domestically available biomass has been proposed as part of the solution to our dependence on fossil fuels. In this respect, we have recently developed catalytic processes to convert biomass derived molecules to liquid alkanes, which could be used as transportation fuel. Alkanes ranging from C₁ to C₆ can be produced by aqueous phase dehydration/hydrogenation (APD/H) of sorbitol (hydrogenated glucose) by a bi-functional pathway. Sorbitol is repeatedly dehydrated by a solid acid (SiO₂-Al₂O₃) or a mineral acid (HCl) catalyst and then hydrogenated on a metal catalyst (Pt or Pd). Larger liquid alkanes ranging from C₇-C₁₅ can be produced by APD/H of larger carbohydrate-derived molecules. The biorefining of sugars to alkanes plus CO₂ and water is an exothermic process in which the products retain approximately 95 % of the heating value and only 30 % of the mass of the reactant.

9-15

Modeling of Long Chain Branching: Application to New Products From Gas Phase Reactors

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Abstract pending

9-16

Recyclable Polymerization Catalysts – Silica-Tethered CuBr-Bipyridine Atom Transfer Radical Polymerization Catalysts

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It is well-known that most chemical products made on a moderate to large scale are produced in a process that utilizes solid catalysts, as the use of solid catalysts facilitates easy product recovery and repeated catalyst use. However, a notable exception to this trend exists in the area of polymerization catalysis, where most catalysts are single-use entities. For this reason, they are engineered to give extremely high productivities to achieve low residual catalyst content in the final polymers.

Nonetheless, there are many emerging polymerization technologies that produce unique *new polymers* from *old monomers* that are commercially very attractive. However, many of them, like atom transfer radical polymerization (ATRP), require a large amount of catalyst that must be effectively recovered and ideally recycled to facilitate potential commercial application. Indeed, ATRP is an attractive technology because it allows for the preparation of well-defined polymers such as block copolymers due to the quasi-living/"controlled" nature of the polymerization. Unfortunately, ATRP requires a relatively high catalyst loading that results in significant metal residue in the final polymer. Thus, a recoverable, recyclable catalyst would be a useful advance.

The construction of solid catalysts for polymerization requires different design rules than catalysts for small molecule transformations. In particular, the role of porosity, or a lack thereof, plays a critical role. Here we report our recent studies into the design of recoverable, recyclable ATRP catalysts based on silica supported CuBr complexes of bipyridine and pyridylmethanimine. The roles of synthetic method, catalyst porosity, and ligand structure are evaluated in the catalytic polymerization of methyl methacrylate. Additionally, a new catalyst regeneration method is introduced and an effective, recyclable system for the controlled polymerization of methacrylate monomers is achieved.

9-17

Naturally Chiral Surfaces

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Single crystalline surfaces terminated in structures with kinked steps have inherent chirality. The enantioselective properties of these surfaces have been explored using both temperature programmed desorption (TPD) and Fourier Transform - Infrared Reflection Absorption Spectroscopy (FT-IRAS) measurements. The adsorption of R-3-methylcyclohexanone (R-3-MCHO) has been shown to be enantioselective on the several different kinked Cu surfaces. TPD measurements show distinct, resolvable features associated with desorption from the terraces, steps, and kinks on the surface. The desorption kinetics from the kinks depend on the relative handedness of the adsorbate and the surface. The decomposition of chiral alkyl groups including 2-butyl and 2-methyl-butyl have been studied on the Cu(531) and Cu(643) surfaces. Their decomposition by β -hydride elimination yields a number of products and the product yields have been shown to depend on the relative handedness of the alkyl groups and the Cu surfaces. These results suggest that naturally chiral surfaces can be used for enantioselective chemical processes such as heterogeneous catalysis or separations.

9-18

NO Oxidation Reaction Kinetics on Pt/Al₂O₃ Catalyst

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The oxidation of NO to NO₂ over a supported noble metal component is an important step involved in NO_x abatement techniques, e.g., selective catalytic reduction (SCR) and NO_x storage/reduction (NSR) processes being developed for lean-burn diesel engines to limit their NO_x emission. We demonstrate here the kinetics of NO oxidation reaction on a Pt/Al₂O₃ catalyst. The rate equation for the reaction was determined to be $r = k[\text{NO}]^{1.05 \pm 0.08} [\text{O}_2]^{1.03 \pm 0.08} [\text{NO}_2]^{-0.92 \pm 0.07}$, with k as the rate constant. Thus, the product NO₂ inhibits the forward rate and this makes it imperative to include the influence of NO₂ concentration in any analysis of the kinetics of this reaction. The apparent activation energy was $82 \text{ kJ mol}^{-1} \pm 9 \text{ kJ mol}^{-1}$. We also propose a reaction mechanism consisting of elementary reaction steps that attempts to explain the observed kinetics. We will also discuss our attempts to understand the effects of Pt particle size on this reaction. Our experimental results indicate that the Pt particle size affects the NO oxidation turnover rate (TOR) significantly, with larger Pt particles giving a higher TOR. These findings are crucial to optimize the oxidation of NO to NO₂, and hence the overall NSR process.

9-19

Surface Properties of Supported Gold and Alloy Nanoparticle Catalysts

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We have recently been investigating core-shell assembled gold and alloy nanoparticle catalysts for electrocatalytic oxidation of carbon monoxide and methanol and reduction of oxygen, which are of interest to the development of fuel cell catalysts. The exploitation of the catalytic activity of such materials requires the ability to manipulate the interparticle spatial and surface access properties in controllable ways. This ability is inherently linked to the controllable activation of the nanostructure in terms of size and surface properties. This paper reports recent findings of our investigations in probing the structural and morphological evolution of molecularly-capped metal nanoparticles on different support materials under thermal treatment using atomic force microscopy (AFM), infrared spectroscopy (FTIR), X-ray Diffraction (XRD), and X-ray Photoelectron Spectroscopy (XPS). The results demonstrate that the nanocrystal size and surface binding sites can be controlled by a combination of factors including adhesion, mobility, composition, activation energy and surface tension. These findings have important implications to the design and processing of advanced nanostructured catalysts.

9-20

Electro-catalytically Performance Improvement of La_{1-x}Sr_xCo_{1-y}Fe_yO₃ (LSCF) Cathodes Formed Using the Sol-Gel Method

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$\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_3$ (LSCF) perovskite cathodes display significantly better performance than $\text{La}_x\text{Sr}_{1-x}\text{MnO}_3$ (LSM) because of their high catalytic activity for O_2 reduction, and their very good ionic and electronic conductivity. The sol-gel (SG) method, combined with low processing temperatures, has become increasingly popular for the preparation of metal oxides, due to its advantages of producing materials with high porosity, high surface areas, and homogeneity on the molecular scale. In the present work, SG methods have been employed to synthesize LSCF cathode and 2 mol% samaria-doped ceria electrolyte. The structure phase, morphology, particle size and elemental composition of the SG-LSCF cathodes was obtained using XRD, HRTEM, SEM and WDS. Electrochemistry was carried out in a 3-electrode half-cell configuration, exposed to air. The cathode so-prepared is found to be primarily composed of the LSCF tetragonal phase and its crystallite size ranges between 20-30 nm. SEM showed that the SG-LSCF cathode layer is ca. 30 μm thick and has highly structured channels with thin walls and pores on the order of a micron or less in diameter. HRTEM images of a typical particle indicate the presence of a highly crystalline plane (101) with a few stacked faults. In terms of the cathode's electrochemical performance, the specific area resistance of the cathode at 700 °C averaged to ca. 0.30 $\Omega\cdot\text{cm}^2$, which was substantially better than that obtained by the traditional synthesis technology.

9-21

Liquid-Phase Reductive Deposition as Novel Preparation Method of Hybrid Nano-particulate Catalysts

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Nanoparticles have been received much attention and been widely studied, since its property can change only by the size because of quantum effect when the size is reduced to nanometer level. The decrease of the size is also expected to enhance the catalytic activity, because the decrease in size results in the increase of the total surface area and active sites with unsaturated bonding. Among various methods to synthesize the nanometer-sized particles, the liquid-phase reduction method is one of the easiest procedures, since nanoparticles can be directly obtained from various precursor compounds soluble in a specific solvent. We have taken Ni as an example of target nano-material and then reported that Ni and Ni-Zn nanoparticles with a diameter from 5 to 10nm and an amorphous-like structure were synthesized by using liquid-phase reduction method and that Zn addition to Ni nanoparticles promote the catalytic activity for 1-octene hydrogenation. However, unsupported particles finally lost their activity due to tremendous aggregation because of its high surface activity. In order to solve this problem, we have been developing the selective deposition method onto TiO_2 nanoparticles, named as the liquid-phase selective-deposition method, where TiO_2 plays a role of formation center of Ni nanoparticles as well as protection from aggregation and growth of the particles. In this paper, I will focus on the concept of this method and the detailed formation mechanism of Ni-Zn/ TiO_2 nanocomposite. Nanoparticles synthesized was dispersed and stabilized by the selective deposition onto TiO_2 surface. The particle size was decreased with increasing the amount of Zn added, thus the catalytically active Ni surface area was increased. The selective deposition onto TiO_2 surface

and addition of Zn to the nanoparticle promoted the catalytic activity of Ni-Zn nanoparticle, e.g. the catalytic activity of Ni-Zn/TiO₂ was ca. 10 times higher than that of the unsupported Ni nanoparticles. Ni in the nanocomposite was assigned as metallic, although their surface was oxidized under the atmospheric condition, but Zn and B were deposited as their oxide.

9-22

Active Media Effect on Strength and Durability of Catalysts

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The mechanical wear facilitated by the medium influence can be a principal cause of catalyst losses in many heterogeneous catalytic processes. The direct experiments with MgO, Co-Mo, Ca-Ni-P, Al-Cr-K and other catalysts show that both their strength and durability decrease significantly, sometimes dramatically during catalysis with respect to identical tests in the inert media. The effect has been explained as the thermodynamically predicted result of the mutual influence of solid phase and medium in catalytic process: new bonds arising between them may cause bonds weakening and rupture both in adsorbed molecules and in solid surface (i.e., Rehbinder effect manifestation). In this aspect, catalyst is a victim of its destination. However, the resistance of catalyst granules to wear can be essentially improved by perfecting their technology: selection of optimal size grading of the granule forming particles and strengthening contacts between these particles, using nano-disperse inactive fillers and hydration hardened mineral binders, reducing residual internal stresses, etc. Catalysis assisted rupture of surface bonds may result also in creating new surface adatoms and, correspondingly, in accelerating the surface selfdiffusion and particles sintering, i.e., in the increase in strength, or achieving the same interparticle contacts development and strength at lower sintering temperatures (Catalysis Enhanced Sintering - CES). This has been recently shown both for metals (Fe, Ni) and ceramics (alumina, zirconia, yttria) powder samples.

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Synthesis of Nanosized TiO₂-SiO₂ Complex Particles and Their Photocatalytic Activity

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Titania-silica (TiO₂-SiO₂) nanoparticles were prepared by sol-gel procedure with mix up hydrolyzed titania-sol (TBOT as a titanium precursor) and silica-sol (TEOS as a silica precursor). These nanoparticles were then characterized by X-ray powder diffraction (XRD), transmission electron microscopy (TEM), Scanning electron microscopy (SEM)-energy dispersive X-ray analysis (EDX), X-ray photoelectron spectroscopy (XPS), Ultraviolet-visible (UV-Vis) spectroscopy, Raman spectroscopy and thermogravimetric/differential thermal analysis (TGA/DTA). The analytical results demonstrated that the complex of SiO₂ with TiO₂ can increase the phase transformation temperature of TiO₂ and enhance the thermal stability of TiO₂ structure, no rutile phase was observed for the TiO₂-SiO₂ particles up to 800 °C. The

micrographs of TEM and SEM showed that the $\text{TiO}_2\text{-SiO}_2$ particles had a spherical and a narrow size distribution 60~80 nm. The Raman spectra indicated that the nanoparticles showed highly broadened with the blue shift of the anatase features at lower temperature and the peaks sharpened as the temperature increased. In addition, $\text{TiO}_2\text{-SiO}_2$ particles showed high photocatalytic activity on the photocatalytic decomposition of phenol and its derivatives.

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Formation of PE Nano-Fibers by Catalytic Polymerization and Extrusion at the Nanometer scale on Confined Transition Metal Carbonyls

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The transition metal carbonyls, i.e., $\text{Cr}(\text{CO})_6$, $\text{Mn}_2(\text{CO})_{10}$, $\text{Co}_2(\text{CO})_8$ and $\text{Fe}_2(\text{CO})_9$ (guests) have been anchored and confined into the pore network of siliceous materials (host). These systems exhibited unusual catalytic properties for the low olefins polymerization reactions (1,2). The formation of PE nano-fibers and nanotubes of about 4 to 5 nm diameter, which is similar to the host pores diameter, indicate a reaction and extrusion mechanism occurring at the nanometer scale. The study of these systems by XANES-EXAFS, FTIR, TEM(HREM), ^{29}Si -NMR(MAS) and ^{129}Xe -NMR allowed to explain these results in terms of interaction of the molecular confined species inside the pores with the surface siloxane groups, thus inducing an electron transfer from the sub-carbonyl species to the silica wall. This study should contribute to the design of new catalysts at the nanometer level.