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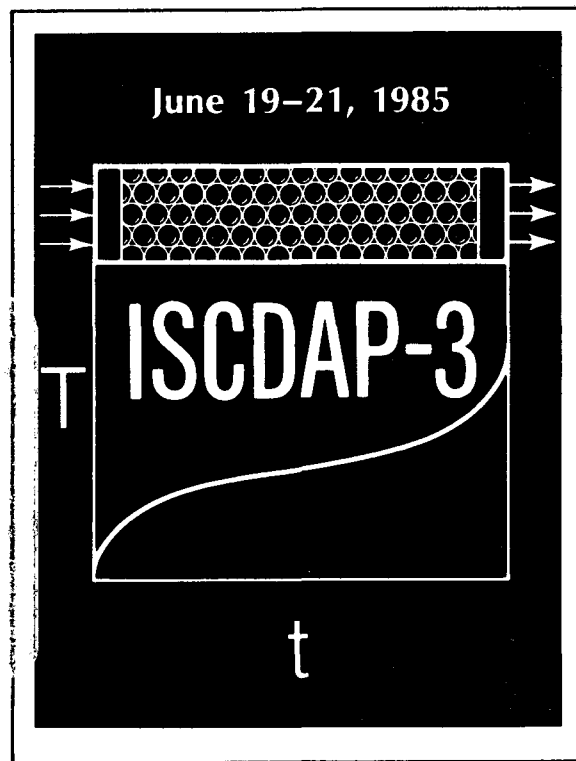
THIRD INTERNATIONAL SYMPOSIUM ON CATALYST DEACTIVATION & POISONING

PROGRAM & ABSTRACTS

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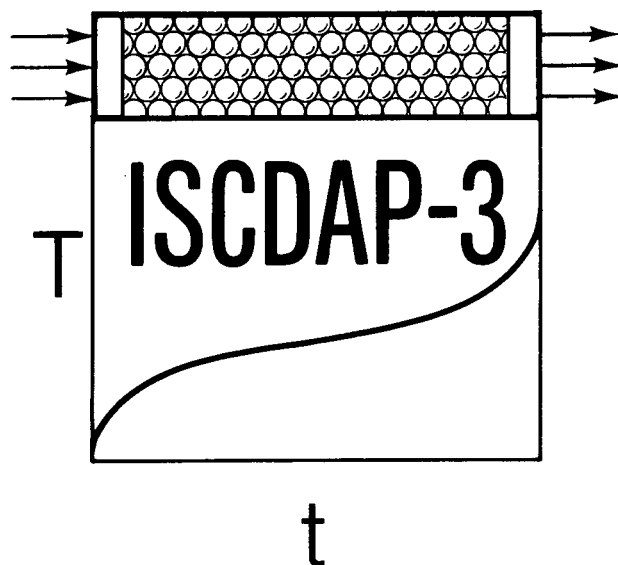
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**THIRD INTERNATIONAL SYMPOSIUM ON
CATALYST DEACTIVATION AND POISONING**

Lawrence Berkeley Laboratory

June 19-21, 1985



**Materials and Molecular
Research Division
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720**

THIRD INTERNATIONAL SYMPOSIUM ON CATALYST DEACTIVATION AND POISONING

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WEDNESDAY MORNING, JUNE 19

- 8:45 Welcome – E.E. Petersen, U.C. Berkeley, LBL
Introductory Remarks – D.A. Shirley, Director, LBL
Morning Chairman: A.T. Bell, U.C. Berkeley, LBL

Theory of Catalyst Deactivation

- 9:00 The Poisoning of Catalysts: Experimental Observations and Modelling –
J.B. Butt, Northwestern University, Evanston, Illinois
- 10:00 The Fouling of Catalysts: Experimental Observations and Modelling –
E.E. Petersen, University of California, Berkeley, California
- 11:00 Coffee Break
- 11:15 The Sintering of Supported Metal Catalysts: Experimental Observations
and Modelling – S.E. Wanke, University of Alberta, Edmonton, Canada
- 12:15 Lunch

WEDNESDAY AFTERNOON, JUNE 19

Afternoon Chairman: J.B. Butt

Bimetallic Catalyst Stability

- 1:30 Characterization of Catalyst Surfaces by Reactive Gas Titration – P.G.
Menon, Chalmers University of Technology, Gothenburg, Sweden
- 2:30 Mechanisms of Stabilization – M.J. Kelley, E.I. DuPont De Nemours and
Co., Inc., Wilmington, Delaware
- 3:30 Coffee Break
- 3:45 The Role of Sulfur on Catalyst Deactivation – J. Oudar, Ecole Nationale
Supérieure de Chimie, Paris, France
- 6:00 Social Hour – The Faculty Club, University of California, Berkeley,
California
- 7:00 Banquet – The Faculty Club, University of California, Berkeley, California
Banquet Speaker: Dr. William E. Siri, LBL – “Adventures in Strange
Places”

THURSDAY MORNING, JUNE 20

Morning Chairman: S.E. Wanke

Chemistry and Physics of Catalyst Deactivation

- 9:00 Deactivation of Enzymes – E. Katchalski-Katzir, The Weizmann Institute of Science, Rehovot, Israel
- 10:00 Deactivation and Poisoning of Fuel Cell Catalysts – Philip Ross, Lawrence Berkeley Laboratory, Berkeley, California
- 11:00 Coffee Break
- 11:15 Deactivation of Homogeneous Catalysts – Barbara Warren, Union Carbide Corp., South Charleston, West Virginia
- 12:15 Lunch

THURSDAY AFTERNOON, JUNE 20

Afternoon Chairman: L.L. Hegedus

- 1:30 Characterization of Carbonaceous Residues on Catalysts – A.T. Bell, University of California, Berkeley, California

Regeneration, Rejuvenation, and Reclamation

- 2:30 Deactivation and Regeneration of Heavy Feed Hydrotreating Catalysts – K. Riley, Exxon Research & Development Laboratories, Baton Rouge, Louisiana
- 3:30 Coffee Break
- 3:45 Redispersion of Metal Catalysts – J. Schoennagel, Mobil Research & Development Co., Paulsboro, New Jersey
- 6:00 Wine Tasting – The Faculty Club, University of California

FRIDAY MORNING, JUNE 21

Morning Chairman: S.E. Wanke

Structural and Chemical Stabilization of Catalysts

- 9:00 Metal Catalysts Supported in Molecular Sieves: Sintering and Poisoning – P. Gallezot, Institute of Catalysis, Villeurbanne, France
- 10:00 Microstructures and Transformations of Supported Catalysts – L.D. Schmidt, University of Minnesota, Minneapolis, Minnesota
- 11:00 Coffee Break
- 11:15 Design of Hydrotreating Catalysts – L.L. Hegedus, W.R. Grace & Co., Columbia, Maryland
- 12:15 Closing Remarks – A.T. Bell, University of California, Berkeley, California

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THE POISONING OF CATALYSTS:
EXPERIMENTAL OBSERVATIONS AND MODELLING

John B. Butt

Department of Chemical Engineering,
Northwestern University, Evanston, Illinois 60201

In the most general sense it is convenient to think of poisoning as the removal of sites from the active catalytic surface by the strong competitive chemisorption of reaction mixture impurities. Poisons can affect single sites or ensembles of sites; significant changes in activity and/or selectivity can thus be caused by poison coverages as low as small fractions of a monolayer.

Systematic investigation of poisoning is of relatively recent history, although the problem has been with us as long as catalysis, of course. Indeed, one of the first observations of poisoning was reported by M. Faraday in 1834 for the suppression of $H_2 + O_2$ on Pt by C_2H_4 .

Some classification as to the fundamental types of poisoning mechanisms is afforded by distinction as to "temporary" or "permanent" and "selective" or "nonselective." One may further make a distinction between homogeneous surfaces and heterogeneous or bifunctional surfaces. Finally, one can attempt a distinction on the basis of differing geometric or electronic effects, although to date this approach has not been generally more rewarding than in other areas of catalysis. The presentation will deal with the analysis of such classifications of poisoning mechanisms through several examples from the literature, both recent and elderly.

A second aspect of the presentation has to do with the interaction of poisoning and chemical process dynamics, particularly the dynamics of chemical reactors. While poisoning is not unique among mechanisms of catalyst deactivation in inducing unsteady state behavior in processes we would like to see as steady state, certain aspects have proven useful in increased understanding of both experiment and simulation. These include particularly systems in which the chemistry is relatively well understood, poisoning is rapid, and there is a substantial difference in the activation energies of the poisoning and main reactions. Again a discussion with respect to selected pertinent literature will be presented with an evaluation of potential future research directions.

THE FOULING OF CATALYSTS:
EXPERIMENTAL OBSERVATIONS AND MODELLING

E.E. Petersen

Materials and Molecular Research Division,
Lawrence Berkeley Laboratory,
and
Department of Chemical Engineering,
University of California, Berkeley, California 94720

Fouling and coking of catalysts and their relationship to deactivation are discussed as separate processes and as processes that occur simultaneously in time. The kinetics of coking and the implication of coke distribution on pore blockage are reviewed. Fouling is defined and measured by a decline in activity of the catalyst for the main reaction. The kinetics of fouling for a number of industrial and industrially related processes are presented in terms of a general correlation based on much of the literature on hydrocarbon reactions. This general correlation is interpreted utilizing a model of the following process. Reforming and catalytic cracking are discussed in terms of the model.

THE SINTERING OF SUPPORTED METAL CATALYSTS:
EXPERIMENTAL OBSERVATIONS AND MODELLING

Sieghard E. Wanke

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The decrease in metal surface area due to growth of metal particles is one of the causes for the deactivation of supported metal catalysts. This growth of metal particles, i.e., sintering, occurs during prolonged use at elevated temperatures and during coke burn-off. Various factors that influence the sintering behavior of supported metal catalysts, such as nature of support, type of metal, sintering atmosphere, impurities, and additives, will be discussed in this paper.

A brief review of supported metal catalyst sintering will be presented, but the majority of the presentation will deal with recent sintering results obtained for Pt supported on various aluminas, magnesias, silicas, silica-alumina, and silicalite. Catalysts, containing 0.5 to 5.0 wt% Pt, were prepared by impregnation or exchange with chlorine-containing and chlorine-free Pt precursors. These catalysts were sintered in H_2 and O_2 at temperatures up to $800^\circ C$, and changes in Pt dispersion were measured by H_2 and CO chemisorption, x-ray diffraction, and transmission electron microscopy. Comparison of Pt dispersions obtained by the different characterization techniques showed that chemisorption, in general, is not a reliable method for determining Pt dispersions. H_2 and CO uptakes were often markedly affected by reduction temperatures and by chlorine and sulfur contents. However, the combination of the three characterization methods yielded reliable information on the effects of sintering conditions on Pt dispersion.

Sintering in H_2 , even at $800^\circ C$, was relatively slow and not very sensitive to the nature of the support. Sintering in O_2 , on the other hand, was very sensitive to the type of support. All catalysts, except those supported on MgO, sintered rapidly in O_2 at temperatures $600^\circ C$. Pt/MgO catalysts displayed amazing thermal stabilities in O_2 , retaining high Pt dispersions even after treatment at $800^\circ C$. Increases in Pt dispersions, i.e., redispersion or regeneration, were also observed for Pt/MgO catalysts during O_2 treatment of chlorine-free as well as chlorine-containing catalysts. Increases in dispersion were also observed for Pt/ γ - Al_2O_3 as a result of O_2 treatment at temperatures $550^\circ C$; however, this behavior was strongly influenced by chlorine content and Pt crystallite size. Only decreases in Pt dispersion were observed for supports other than γ - Al_2O_3 and MgO.

The results of these and previous studies are interpreted in terms of an atomic migration model, i.e., sintering and redispersion results from the migration of atoms or molecules across the support surface. Sintering takes place if only weak local interactions occur between the support and the migrating species. Redispersion can take place if strong localized interactions occur between the migrating species and the support and/or support additives. Speculations regarding the nature of the metal-support interactions during redispersion will be presented.

CHARACTERIZATION OF CATALYST SURFACES BY REACTIVE GAS TITRATION

P. Govind Menon

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Chalmers University of Technology, S-41296 Gothenburg, Sweden

The chemical composition of a solid catalyst surface can be quite different from that in the bulk. Either a surface depletion or a surface enrichment can occur during the preparation or pretreatment of the catalyst, during the catalytic reaction, or due to mishaps in operation. Despite the development of several powerful physicochemical characterization techniques for probing the exact composition of multi-phase solid surfaces, specific chemisorption of gases still continues to be a simple, elegant, versatile, and inexpensive method for this purpose. Hence this review highlights some of the more recent achievements of this good old technique and its modern adaptations. The emphasis here will be on reactive gas titrations of the surfaces of supported-metal and mixed-oxide catalyst systems that are commonly used in industry.

The illustrative examples discussed include iron catalysts for ammonia synthesis and Fischer-Tropsch synthesis, Pt-Re/Al₂O₃ catalysts for catalytic reforming, Pt-Rh, Pt-Ru/SiO₂, Rh/TiO₂, Ag/TiO₂, Pt₃Sn and Cu-Ni, and multi-component molybdates. In some cases, supporting or complementary information can also be obtained by temperature-programmed reduction/desorption (TPR/TPD) of/from the same catalyst sample in the same equipment. The TPD of ammonia or n-butylamine can give the total number of acid sites and, more importantly, the acid-strength distribution of these sites in acidic catalysts like silica-alumina or molecular sieves.

Reactive surface gas titrations can be used not only for typical dispersion studies of the catalytically active material on the support surface as discussed above, but also for obtaining more in-depth information on the catalyst system. For instance, the selective and nonselective parts of the lattice oxygen in oxide or molybdate catalysts for selective oxidation of olefins can be determined by propylene pulse titration of the catalyst surface (in the absence of air or oxygen) until all the available lattice oxygen of the catalyst is reacted off to form acrolein, CO₂, and H₂O. Similarly, the nature and quantity of adsorbed or active intermediates on a catalyst surface under actual reaction conditions can be estimated by sweeping or "reactive scavenging" of the surface with a suitable reactant.

Compared to conventional chemisorption techniques, the main advantages of surface titration are rapid equilibration, increased sensitivity, fair immunity to the effects of support or contaminants, and relative insensitivity to the so-called strong metal-support interaction (SMSI). Complications may arise, however, from nonspecificity in chemisorption, variable chemisorption stoichiometry, unsuspected surface enrichment of a component or a contaminant, etc. These should be recognized as peculiarities or limitations of the catalyst system, not as examples to be cited for finding fault with the gas titration technique as such.

MECHANISMS OF STABILIZATION

Michael J. Kelley

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and

Dady B. Dadyburjor

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The most prominent bimetallic catalysts are descended from monometallic parents; the chief virtues attributed to these offspring are improved stability (life) and selectivity. The selectivity improvement may arise from enhanced stability, permitting operation under desirable but otherwise intolerable conditions. It is therefore natural to discuss deactivation in terms of the loss of "bimetallicity" coupled with processes seen in monometallics, such as sintering and coking discussed by other speakers. Proposals for what constitutes bimetallicity include:

Alloy formation, where the primary and modifier metals are combined in the same particle. Reduced carbon deposition is attributed to atoms of a weakly adsorbing modifier metal reducing the number of adjacent strongly adsorbing primary metal atoms on the catalyst surface, preventing formation of large organic entities that might be coke precursors. Another alloy effect can be formation of stronger bonds between the two metals than either alone, making formation of the mobile species in sintering less energetically favorable, thereby reducing the rate of sintering. Deactivation would then arise from operating conditions that overwhelm these effects or from breakdown of the alloy.

Multifunctionality, where the modifier metal is not necessarily combined with the primary metal, but rather contributes a catalytic activity of its own that intercepts some element of the deactivation sequence of the primary metal. For example, carbon deposition can be reduced by conversion of coke precursors to innocuous species. Perceptible deactivation of the total catalyst begins when the modifier has lost sufficient activity that it can no longer protect the primary metal.

Trapping, where the modifier metal is dispersed substantially uniformly in the support surface and binds more strongly to the primary metal than does the support itself. Formation of mobile species during sintering is therefore less energetically favorable. Mobile species that do form have an increased probability of becoming anchored on the support rather than contributing to the growth of another metal particle. Of course, the modifier element must be free from unwanted catalytic effects of its own. Deactivation can come about by loss, aggregation, or poisoning of the modifier metal trap sites.

Poisoning, where the modifier metal eliminates some activity of the primary metal for unwanted reactions or makes the catalyst less susceptible to take up some deactivating species, either on the metal or the support. Deactivation would then arise from loss or saturation of the modifier.

"Glue," where the modifier metal is selectively present at the interface between the support and the primary metal, anchoring the primary metal and making it more stable against sintering. It is a special case of trapping, where the trap element is not present to any extent in the support surface away from the particles. Deactivation begins when the primary metal particles become separated from the glue.

A first step in studying deactivation is establishing the catalyst initial state, after pretreatments but before reaction, to know what bimetallic effect(s) are operating. Such a well-defined, uncontaminated material should provide an excellent object for modern spectroscopic methods. However, controversy persists even as to the oxidation state of the modifier metal for extensively studied systems (e.g., Pt-Re). This state of affairs is discouraging for carrying out the next steps--repeating the characterization at successive points in the catalyst's life cycle. The most promising results are coming from in situ techniques, especially x-ray absorption spectroscopy and transmission electron microscopy.

Hopefully this can be somewhat alleviated by careful modelling of potential bimetallic effects and deactivation mechanisms--how the alloying, particle size, particle size distribution, and carbon deposits change with time. The goal here is to anticipate cases where different mechanisms will lead to widely different catalyst final states to enhance the prospects for successful characterization experiments. Such efforts do not yield results soon or easily, but we are encouraged by the progress made so far.

THE ROLE OF SULFUR ON CATALYST DEACTIVATION

J. Oudar

Ecole National Supérieure de Chimie,
Paris, France

For investigating the role of sulfur on hydrogenation reactions, catalytic model experiments have been performed on single crystals of platinum at pressures near atmospheric. The surface was characterized before and after the reaction by AES and LEED.

In a first series of experiments, the H₂-D₂ equilibration rate was measured on the main low index planes as a function of the surface coverage by sulfur.¹ The deactivation curves so obtained were characterized by a non-linear behavior. It was also observed that sulfur strongly modifies the activation energy and the mechanisms of hydrogen dissociation and recombination occurring on the sites remaining free of sulfur.

In a second series of experiments, butadiene hydrogenation and H₂-D₂ equilibration were investigated together.² In the steady state conditions the surface was covered by a monolayer of butadiene. It was observed that (i) sulfur decreases in the same ratio as the rate of butadiene hydrogenation and the equilibration rate; (ii) the deactivation curves for both reactions were linear as a function of sulfur coverage, indicating that each sulfur atom poisons one site for hydrogen dissociation; (iii) the activation energy for both reactions and the selectivity toward butene and butane were not affected by sulfur, indicating no change in the mechanisms of the reactions occurring on the sites remaining free of sulfur.

The deactivation curve has been used for determining the surface coverage of sulfur during the hydrogenation of butadiene in gas mixtures containing well-controlled amounts of H₂S. From the adsorption isotherm so obtained, it is concluded that the butadiene molecules, adsorbed in the steady state conditions of hydrogenation, strongly decrease the binding energy of sulfur on platinum (15% to 20%) and totally suppress the interactions between adsorbed sulfur atoms.

As a general conclusion of this study, it appears that the deactivation behavior of one impurity such as sulfur strongly depends on the surface coverage by the hydrocarbon during the catalytic reaction. Such a conclusion is relevant to other systems involving unsaturated hydrocarbons.

References:

1. C.M. Pradier, Y. Berthier, and J. Oudar, *Surf. Sci.* 130 (1983), 829.
2. S. Pinol, Y. Berthier, and J. Oudar, *C.R. Acad. Sci. Paris* (1985), in press; S. Pinol, *These de 3eme cycle*, Paris, March 1985.

DEACTIVATION OF ENZYMES

E. Katchalski-Katzir

The Weizmann Institute of Science,
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Abstract not received in time for inclusion in program.

DEACTIVATION AND POISONING OF FUEL CELL CATALYSTS

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A fuel cell is an electrochemical energy conversion device that converts chemical energy to electrical energy without the use of an intermediate mechanical (or Carnot) cycle. At present, all fuel cell devices approaching real practice convert only hydrogen directly, and not any form of hydrocarbon. This is not a fundamental limitation but a practical limitation due to the absence of a catalyst that provides direct conversion of hydrocarbons at a practical rate (and cell potential). With the exception of special purpose fuel cells that use pure hydrogen as fuel (e.g., space and deep-sea vehicles), fuel cells have a fuel conditioning (steam reforming and water gas shifting) unit that converts a hydrocarbon fuel into a hydrogen-rich gas that is fed to the electrical generating unit. Typical hydrocarbon fuels in use are natural gas, naphtha, and methanol. Heavier fuels or coal gases are problematic and are the subject of research and development designed to broaden the fuel range for future fuel cell technology. In this paper, we will not discuss the problems of catalyst deactivation in the fuel conditioning unit, since these are conventional catalysts and reactors that are covered by other papers in this symposium. The discussion here will be restricted to the unique aspects of catalysts in the electrical generating unit of fuel cells.

Fuel cell catalysts suffer from deactivation and poisoning phenomena that are either identical to or strongly analogous to the processes that occur in heterogeneous catalysis. As in conventional catalytic reactors, fuel cell performance is degraded by poisoning from impurities, loss of surface area of noble metal, and physical deterioration of the catalyst structure. Unlike conventional catalytic reactors, where some catalyst regeneration capability is usually designed into the system, the fuel cell catalyst is an integral part of the physical structure of the electrical generator, and there are at present no designs that are able to employ catalyst regeneration. Therefore, catalyst deactivation and poisoning phenomena are even more serious technological problems in fuel cells than in conventional reactors.

The deactivation and poisoning phenomena to be reviewed in detail in this paper are: the poisoning of the anode (fuel electrode) catalyst by carbon monoxide and hydrogen sulfide; the deactivation of the cathode (air electrode) catalyst by sintering; and the deactivation of the cathode by corrosion of the support. The fuel cell technology discussed in the context of these phenomena is the phosphoric acid fuel cell. The operating conditions for this technology are typically 180-210°C, 95-99% acid, and in pressurized versions 50-120 psig.

The anode catalyst is Pt supported on a conductive, high area carbon black, usually at a loading of 10 w/o. This catalyst is tolerant to some level of carbon monoxide or hydrogen sulfide or both in combination, the level depending on temperature and pressure. Carbon monoxide poisoning has been

studied extensively, including detailed adsorption studies at various temperatures and pressures. Based on these studies, predictive models have been developed that effectively predict anode tolerance to carbon monoxide. Much less is known about hydrogen sulfide poisoning, and at present the tolerance levels can only be described parametrically. Typical tolerance levels are 2% CO and 10 ppm H₂S.

The cathode catalyst is typically Pt supported on a graphitic carbon black, usually a furnace black heat-treated to 2700°C. The Pt loading is typically 10 w/o, and the dispersion (or percent exposed) as prepared is typically 30%. The loss of dispersion in use depends on the operational parameters, most especially the cathode potential history; i.e., higher potentials cause more rapid decrease in dispersion. Relatively few fundamental studies of this phenomenon have been published, and those that are available are contradictory; the mechanism of loss of dispersion is not well known. The graphitic carbon support corrodes at a finite rate that is also potential dependent. Support corrosion causes thickening of the electrolyte film between the gas pores and the catalyst particles, which in turn causes increased diffusional resistance and performance loss. In addition, support corrosion may also cause loss of Pt into the separator. Support corrosion appears to be the life-limiting factor for phosphoric acid fuel cells.

DEACTIVATION OF HOMOGENEOUS CATALYSTS

Barbara Knight Warren

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Homogeneous catalytic reactions of industrial importance, in contrast to heterogeneous systems, are relatively recent and comprise a small fraction of industrial reactions. Homogeneous reactions, however, can have significant advantages. The causes and mechanisms of heterogeneous catalyst deactivation are well studied and include poisoning (e.g., by sulfur), fouling (by coking or by impurities), sintering or thermal degradation, and loss of catalyst by attrition or volatility of an active component. Catalyst deactivation mechanisms for homogeneous processes are not as well reported but present analogies to those of heterogeneous processes. As in heterogeneous catalysis, process design and conditions affect catalyst deactivation. Types of homogeneous catalyst deactivation include poisoning, loss of catalyst through cluster formation, precipitation or volatility, ligand degradation, formation of stable carbon-containing species (analogous to coking), and loss of the proper oxidation state of the catalyst metal.

Specific catalyst deactivation mechanisms for several industrially important homogeneous reactions will be reviewed, including those for hydroformylation with cobalt, phosphine-modified cobalt, and rhodium; conversions of syn gas to organic products with cobalt, rhodium, and ruthenium; catalytic hydrocyanation of olefins by nickel complexes; asymmetric hydrogenation with rhodium; the palladium-catalyzed Wacker process; and homogeneous Ziegler-Natta chemistry. The structure and stoichiometry of homogeneous catalysts are better known and more easily studied than the active components in heterogeneous catalysts; thus specific modifications of homogeneous catalysts are easier (for instance by ligand modification). Ways to avoid or reverse homogeneous catalyst deactivation will be discussed, and a wish list for new developments will be presented.

CHARACTERIZATION OF CARBONACEOUS RESIDUES ON CATALYSTS

Alexis T. Bell

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and
Department of Chemical Engineering, University of California,
Berkeley, California 94720

During the processing of feedstocks containing hydrocarbons or carbon monoxide, metal catalysts often accumulate a carbonaceous deposit. Such deposits can result in the reconstruction of the metal surface, loss of surface sites, encapsulation of metal particles, detachment of metal particles from their support, and pore blockage. The structure and composition of the carbonaceous deposits are a strong function of feedstock composition, metal composition, and reaction conditions. Moreover, with time on stream less refractory forms of carbon or coke gradually transform into more refractory forms. The objective of this talk will be to review the physical techniques that have been developed in recent years for characterizing the structure and composition of carbon deposited on the surface of metal-containing catalysts. Some insights regarding the pathways by which carbidic carbon is converted to graphite, and the pathways by which unsaturated hydrocarbons are converted to coke, will also be presented.

DEACTIVATION AND REGENERATION OF HEAVY FEED HYDROTREATING CATALYSTS

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and

B.G. Silbernagel

Exxon Research and Engineering Company, Annandale, New Jersey

Pilot plant studies, laboratory chemical treatments, and chemical and magnetic resonance observations have been used to trace the deactivation of hydrotreating catalysts during the treatment of heavy, metals-bearing feeds as well as during attempts to regenerate the catalysts by heteropolyacid treatments. In hydrotreating service on light feeds with low metals contents, deactivation proceeds slowly, and the catalyst can be regenerated by mild oxidation of the coke that accumulates on the catalyst surface. For heavier feeds, deactivation proceeds more quickly, and oxidative regeneration in the presence of the co-deposited metals from the feed leads to sintering of the catalyst. In order to arrive at an optimum catalyst utilization strategy, it is important to have an understanding of the microscopic surface chemistry of the deposited coke and metals on the catalyst. To achieve this, a series of pilot plant runs were made to study the effect of feed composition on deactivation rate using three specially selected feedstocks. A high metals, heavy crude was treated with hydrofluoric acid (HF) to selectively remove Ni and V and was also deasphalted with n-pentane to reduce Conradson Carbon residue. Spent catalysts from hydrodesulfurization activity maintenance runs with these feeds, using a small pore Co-Mo/Al₂O₃ catalyst, were used to study the chemistry of the carbon and vanadium deposits. Activity results and deposit profile indicate that carbon deposition controls deactivation in the early stages of a run, while long term deactivation is influenced by coke formation as well as a metals-related pore plugging due to the formation of vanadium sulfide crystals with the approximate composition V₂S₃.

These catalysts can be regenerated, in principle, if deposited metals can be removed from the catalyst prior to the oxidative regeneration step. Historically, acid treatments of catalysts have been applied for metals removal, and, in fact, metals recovery has been affected by acid dissolution of the support. These treatments tend to be nonselective with respect to the removal of metals; i.e., substantial amounts of the catalytically active metals are removed along with the vanadium and nickel that is deposited on the catalyst from the feed. There is also a tendency for the acid treatment to attack the alumina support. We find that treatments with molybdenum heteropolyacids are much more selective with respect to metals removal. Under the appropriate conditions, virtually none of the molybdenum is removed from a Co-Mo catalyst, and approximately 60% of the cobalt remains. The support integrity remains good, with minimal reductions in the crush strength of the catalyst. Tracing the changes in metals chemistry of the vanadium species with nuclear magnetic resonance and electron spin resonance, we find that the vanadium sulfide form is most readily removed, followed by a vanadium surface species, and finally isolated vanadium ions occupying defect sites in the alumina support. Since these latter ions are good candidates for initiation of support sintering upon thermal treatment, it is important that the catalyst be carefully demetallized prior to oxidative regeneration.

REDISPERSION OF METAL CATALYSTS

J. Schoennagel

Mobil Research and Development Co.,
Paulsboro, New Jersey

Abstract not received in time for inclusion in program.

METAL CATALYSTS SUPPORTED IN MOLECULAR SIEVES: SINTERING AND POISONING

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Metal catalysts supported in zeolites include a large variety of clusters of different nuclearities, encaged or occluded in the porous framework. The structural and chemical stabilization of the metal, the redispersion capability, the resistance to poisoning, and the catalytic properties depend upon several unique physical features of these catalytic systems, viz.:

1. The metal atoms facing the cage walls are accessible only to hydrogen, whereas the atoms facing the cage or pore apertures can adsorb all reactant and poison molecules. This partition of the surface may have obvious consequences on the kinetics of the catalytic reactions and on the resistance to poisoning.
2. Selective adsorption of reactant molecules can also be achieved with bi-metallic clusters. Thus combining group VIII and group VIB elements in the same cluster (e.g., Pt-Mo) results in a synergetic effect in hydrocarbon and CO conversions and an improved resistance to sulfur.
3. Metal clusters are more resistant to sintering when they are trapped in cages and cannot migrate as a unit. However, atomic migration may occur depending upon the nature of the metal, the gas phase, and the pore structure.
4. Redispersion of the metal phase might occur under milder conditions than with other metal-supported catalysts, provided the metal particles are still occluded in the zeolite matrix, which favors oxydo-reduction and transport processes. Examples of oxidative dissolution of metal particles involving complexation, transport, and redispersion in cages are given.
5. The electronic structure of nanometer-size clusters is different from that of larger particles because of intrinsic size effects and environmental effects. This may account for some peculiar catalytic properties and poison resistance of metal clusters in zeolites.

MICROSTRUCTURES AND TRANSFORMATIONS OF SUPPORTED CATALYSTS

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Catalyst activation and deactivation processes involve alterations in the microstructure of the catalyst. This could involve changes in phases, crystal planes exposed, site coordination, defects, supports, and particle-support interactions. Until recently these phenomena could only be inferred from activity and surface area measurements, but high resolution electron microscopy and other analytical techniques now permit direct observation of all of these phenomena.

This talk will summarize the experimental and theoretical situation with regard to catalyst microstructures and microstructure transformations of noble metal catalysts on oxide supports. Use of samples in powder and planar form will be summarized, and experimental procedures involving sample transfer and in situ methods of catalyst characterization will be discussed.

Recent TEM and XPS studies of sintering and redispersion of noble metals in H_2 and O_2 environments will be summarized. Phases and microstructures in sulfidation and regeneration of noble metals and Mo catalysts will be considered. Effects of support alterations by volatilization of SiO_2 in H_2O and methods of preparing Pt particles with specific orientations and crystal planes will also be summarized.

These results will be discussed in terms of thermodynamics, metastability of microstructures, and transport processes leading to catalyst activation and deactivation.

DESIGN OF HYDROTREATING CATALYSTS

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The mathematical modeling of fixed-bed hydrotreating catalysts will be discussed, with particular emphasis on the optimal design of hydrode-metallation catalyst geometries and pore structures.

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