Analytical Electron Microscopy of Bimetallic Catalysts

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Charles E. Lyman
Lehigh University

Executive Summary

The following pages summarize the accomplishments, publications, and reception of this program in the catalyst and microanalytical communities. The project, which began in 1986, was renewed twice to give a total of 10+ years of effort including extensions beyond that formal grant period. Initially the research covered a wide range of catalysts, but later in the program, we prepared and optimized a highly active catalyst for low-temperature NO abatement in fossil fuel power plants. The program supported the work for two masters degrees, two Ph.D. degrees, and two post-doctoral years. Under this program, the PI and his associates published 23 archival journal articles, 18 extended abstracts in conference proceedings, and 5 books/chapters.

A major scientific discovery was made during the years 1990 to 1995. This result was the demonstration that thermodynamic principles operate for distributed systems of alloy nanoparticles supported in ceramic pores just as they do for bulk alloys. Surface diffusion and vapor transport replace bulk diffusion as the mechanism for atomic migration. Thus, particles filling ceramic pores, separated by over 100 times their 5-nm average diameter, have been shown to closely conform to equilibrium phase diagrams. The materials science of such distributed alloy systems points to entirely new methods of synthesizing particulates with specific, designer properties.

The above discovery was obtained using the composition-size distribution diagram, pioneered by this group, to detect when particles are single phase or multiphase. Quantitative measurements of sub-10-nm alloy particles was only possible using an ultra-high vacuum field-emission scanning transmission electron microscope with exceptional x-ray collection capabilities. The composition-size diagram also exhibits practical uses in alloy catalyst development. By correlating catalyst test results for a particular reaction with the catalyst microstructure as revealed by the composition-size diagram, fingerprints for active and in-active catalysts can be obtained. The composition-size diagram reveals both alloy phase separation and surface segregation in alloy nanoparticles.

The most practical result from this program is the development of a new catalyst for NO abatement at temperatures under 300°C. This catalyst has good sulfur tolerance when operated in simulated power plant flue gas. The DOE work in this area led to new funding from a consortium of electric utilities for the commercialization of a similar NO reduction catalyst.

During the course of the program, several innovations in microanalytical instrumentation and technique were developed specifically for analysis of catalytic nanoparticles. New designs for improved nanoparticle elemental sensitivity were proposed and accepted by the manufacturer of Lehigh's new VG HB-603 analytical electron microscope. New tests for assessing elemental sensitivity have been devised and used to encourage the manufacturer to build the most sensitive analytical electron microscope in the world.

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Analytical Electron Microscopy of Catalyst Promoters, Poisons and Active Species (1986-1990)

Prof. Charles E. Lyman, PI
Prof. Harvey G. Stenger, Jr., faculty associate
Mr. J. S. Hepburn, research assistant

Accomplishments for the Period (1986-1990)

1. First quantitative measurements of noble metal distributions in alumina monoliths.

The first quantitative microanalysis studies of noble metal co-impregnation processes was accomplished using wavelength-dispersive x-ray spectrometry in an electron probe microanalyzer (EPMA). Fine details of Pt, Rh, and Pd distributions across alumina monolith walls were measured with an analytical sensitivity of about 0.05 wt% metal and a spatial resolution of 10 μm [5-13].

2. First direct elemental imaging of small metal particles poisoned by sulfur.

A Pd/alumina catalyst was intentionally poisoned by SO_2 and analyzed in the analytical transmission electron microscope (AEM). A high-resolution x-ray map was obtained showing sulfur preferentially located on the Pd particles [1]. However, it was noted that the sulfur often could be removed by the electron beam, which prompted the development of a new method for such studies described below [2]. In another catalyst system, sulfur was found to be located directly on Rh particles by x-ray mapping. The energy of the electron beam did not appear to overcome the adsorption of the sulfur to 3-nm diameter Rh particles [13].

3. First analysis of surface species on Co/La/alumina catalyst.

Elemental mapping using x-ray emission spectrometry was used to determine appropriate locations for analysis of surface species on this catalyst. Scatter diagrams for the various elements allowed surface compositions to be determined [4]

4. Development of analytical electron microscopy methods.

For some years it has been realized that further improvements in AEM instruments would greatly benefit catalyst research. During this period specific tests were developed to understand the design parameters necessary to develop an improved analytical electron microscope [30-36].

Analytical Electron Microscopy of Catalyst Preparations (1991-1993)

Prof. Charles E. Lyman, PI
Prof. Harvey G. Stenger, Jr., faculty associate
Dr. Jeffrey S. Hepburn, post-doctoral associate
Mr. Rollin E. Lakis, research assistant

Accomplishments for the Period (1991-1993)

1. Catalytic testing facility brought to the electron microscopy laboratory.

A new catalyst testing facility was built to analyze gas flows before and after contact with the catalyst bed in micro-reactor [21]. This facility greatly improved our group's ability to correlate the microstructure of a catalyst with its useful properties. Very few catalyst testing facilities are intentionally located within close proximity of an electron microscopy laboratory for rapid analysis of catalysts after reaction studies.

2. New scheme for immobilization of surface species for AEM analysis.

After many trials, a method was developed to lock mobile species in place for analysis [14]. This is especially a problem for the alkali metals, often used as promoters, as well for poisons such as sulfur. During earlier attempts at such analysis, some loss of sulfur was noticed [2], but by coating the catalyst surface with a 10-nm thickness of Cr, excellent results were obtained [14, 39]. This work was accomplished in cooperation with Dr. K. Reuter of Union Carbide Corporation.

3. New method for electron probe microanalysis of porous materials.

One of the difficulties in the analysis of supported metal catalysts is that the support material is intentionally porous to maintain a small metal particle size. However, x-ray microanalysis of bulk specimens in the EPMA requires the specimen to be flat-polished and non-porous. The problem has been attacked sporadically but never actually solved. In this work a correction factor is proposed to deal with such analyses [40].

Analytical Electron Microscopy of Bimetallic Catalysts (1994-1998)

Prof. Charles E. Lyman, PI
Prof. Harvey G. Stenger, Jr., faculty associate
Dr. Rollin E. Lakis, post-doctoral associate
Dr. Yeping Cai, post-doctoral associate

Accomplishments for the Period (1994-1998)

This work is important because the nature of small Pt/Rh particles varies widely as a function of preparation method and process conditions (temperature and gas environment). By a systematic study of the Pt/Rh catalyst, we learned how to design and optimize this catalyst for the low-temperature selective catalytic reduction of NO.

1. Successful low-temperature NO reduction using a new Pt-Rh alloy catalyst.

Impregnations Pt and Rh chloride into gamma-alumina, to obtain about 1 wt% metal loading, were examined by AEM and tested catalytically for NO reduction activity. Average metal content within the particles is given as 60/40 for 60% Pt and 40% Rh. Optimized Catalyst 95/5 contained only 5 wt% Rh in the alloy particles, yet this catalyst produced an order of magnitude activity improvement over pure Pt.

Catalyst 60/40.	Pt impregnated - oxidized at 500°C - Rh impregnated - reduced at 300°C
Catalyst 75/25.	Rh impregnated - oxidized at 500°C - Pt impregnated - reduced at 300°C
Catalyst 95/5.	Pt impregnated - oxidized at 500°C - Rh impregnated - reduced at 300°C

The catalytic test results showed that both Catalyst 75/25 and Catalyst 95/5 had greater activity for NO reduction than either pure Pt or pure Rh, while Catalyst 60/40 had an activity midway between pure Pt and pure Rh. This synergistic effect can be seen in Figure 1. These experiments helped to formulate a mechanism for the reaction taking place at the surface of the catalyst. It is proposed that the surface of the catalyst is populated by both Pt and Rh atoms in close proximity to one another. The catalytic action is assumed to be due to the selective adsorption of H₂ to the Pt atoms which are located very near to the sites where NO is adsorbed to the Rh atoms. The 95/5 catalyst was also superior for NO reduction with CO [15-24].

2. "Composition-size diagrams" – a new tool to identify active catalysts.

Not all alloy particles are alike in size or composition, so the mere quoting of a particle composition or particle diameter does not provide sufficient characterization of the particle population. By plotting the elemental composition of a metal particle against the size of that particle, an important characterization tool has been developed for the determining the microstructure of sub-10-nm alloy catalyst particles [19, 20, 22]. Analysis of at least 50 randomly-selected particles is necessary to provide the minimum statistics for characterization. At present this analysis can only be accomplished by manually taking data on a particle-by-particle basis. The first such analysis of sub-10-nm particles was obtained by our group in 1990 [10]. Since that time this characterization tool has been used in DOE-sponsored research and consulting projects covering half a dozen alloy catalyst systems (for example, see [27]).

3. First observation of phase separation in Pt-Rh at 300°C.

Most equilibrium phase diagrams for Pt-Rh indicate a continuous isomorphous solid solution across the diagram. Theoretical predictions of a miscibility gap are dotted in below 700°C for some diagrams, but until now there has been no data in Pt-Rh to support such predictions. Since the Pt-Rh particles are formed in alumina pores, surface effects are expected to be less than for free-standing particles. Thus, it is conceivable that these small particles (< 10 nm) can approach equilibrium. The phase separation is clearly seen in the 60/40 catalyst and in the catalysts prepared by co-impregnated of the two metals [20].

4. First observation of surface segregation in Pt-rich nanoparticles.

The composition-size diagrams for the most active catalysts, Catalysts 75/25 and 95/5, show that the smaller particles appear to be richer in Rh than the larger particles. This is in contrast to the Rh-rich particles of the 60/40 catalyst where the distributions appear to be gaussian and random in both size and composition. The non-random distribution of the Pt-rich particles has been shown to be an indication of surface segregation of Rh [17, 18]. This surface segregation was checked by comparing the measured composition size diagrams to calculated diagrams and by measuring the Rh content in steps across a 10-nm particle. These measurements showed that the most active catalysts for NO reduction were comprised of sub-10-nm Pt-rich particles with about 0.5 monolayer of Rh on the particle surface. This is the first analysis of surface segregation in sub-10-nm diameter particles with the AEM.

5. CO oxidation over Pt-Rh catalyst.

A separate batch of Pt-Rh/alumina catalyst, of nearly the same composition as was used for NO reduction, was succesful for CO oxidation [23]. In the latter case, the gas ratios were adjusted to obtain the desired synergistic effect. A synergistic alloying effect again was obtained, however, the magnitude of the improvement over the pure metals was about 10% rather than the order of magnitude observed for the NO-H₂ reaction.

6. Sulfur poisoning characteristics.

Our NO reduction catalysts were tested for sulfur tolerance by adding SO₂. For the NO-CO reaction, the pure metal catalysts were exposed to 100 ppm of SO₂. This caused the NO reduction activity to decrease by factors of 3 and 4 compared to pre-poisoning conditions for pure Rh and pure Pt, respectively. The alloy catalysts were exposed to 500 ppm of SO₂. A Rh-rich alloy catalyst suffered about the same activity loss as pure Rh, but the synergistic 95/5 catalyst suffered the largest decrease in reaction rate by dropping to one-sixth of its pre-poisoning value. Later experiments, with more realistic gas compositions (described below) and a different support material, showed that NO reduction activity could be maintained even when 400 ppm of SO₂ is added to the gas flow [unpublished work, 1998].

7. Commercial development of NO catalysts.

Since the conclusion of this program, we have received funding from a group of electric utilities to develop a commercial low-temperature SCR catalyst that can be applied to existing power plants at minimal cost. Our previous work (above) was under "pure gas" conditions where the only reactant gases were NO and H₂ in an He carrier. We have used our knowledge of alloy catalyst microstructure to design a catalyst that can operate in a realistic flue gas composition of 5% O₂, 13% CO₂, 8% H₂O, 400 ppm NO, and 400 ppm SO₂. This catalyst provides good conversions of NO, with little N₂O formation at temperatures below 200°C [unpublished work, 1998].

8. Analysis of sub-1-nm particles in Pt-Re reforming catalysts.

A small amount of DOE funding was used for the purchase of instrument time for a visiting scientist from Norway, Baard Tøtdal. His project was to analyze a commercial Pt-Re reforming catalyst after various drying procedures. This catalyst is well-known for its extraordinarily small metal particle sizes and is difficult to observe in the electron microscope. Not only did we observe the particles in annular dark-field mode in the STEM, but the composition of the particles was measured down to particle sizes less than 1 nm [28, 29]. These are smallest particles ever measured by x-ray emission spectrometry in the electron microscope.

Figure 1. Correlation of catalytic activity with catalyst microstructure. The 95/5 catalyst (95%Pt / 5%Rh) exhibits better low-temperature activity for NO reduction than pure platinum. Activities of these catalysts decrease from the 95/5 catalyst to the 17/83 catalyst.

Equipment Purchased Under this Grant

1. Computer control system for JEOL 733 electron microprobe, \$35,000 contribution from this contract.
2. Fourth wavelength-dispersive spectrometer for JEOL 733 electron microprobe, \$6,000 contribution from this contract.
3. New software for parallel-collection EELS system, \$2,000 contribution from this contract.
4. Front surface secondary electron detector for VG HB-603 STEM, \$5,000 contribution from this contract.
5. Automated catalyst testing facility, about \$6,000 from this contract.

Notes on Key Personnel

Charles Lyman, PI.

President of Microscopy Society of America, 1991

Acting Chair of Dept. of Materials Science and Engineering, Fall 1998

President of Microbeam Analysis Society, 1999

Harvey Stenger, Jr., faculty associate

Dean of Engineering and Applied Science, 1993-present

Jeffrey Hepburn, Ph.D student and post-doc

Group Leader, Ford Research Laboratory, Dearborn, MI

Rollin Lakis, Ph.D student and post-doc

Manager of Electron Microscopy, University of Pennsylvania, Philadelphia, PA

Publications

Structure-Property Relationships in Catalysts

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Instrumentation and Methodology for Nanoparticle Analysis

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Books and Book Chapters Related to this Program

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Recent Related Sessions Chaired

- Symposium co-chair: "Electron Microscopy of Catalysts," 12th International Congress on Electron Microscopy, Seattle, 1990.
- Symposium chair: "Compositional Imaging in the Electron Microscope," EMSA Presidential Symposium, 49th Ann. Meeting of the Electron Microscopy Society of America, San Jose, CA, 1991.
- Symposium co-chair: "Clusters, Nanoparticles, Fullerenes, and Related Structures," 13th Int. Cong. of Electron Microscopy, Paris, 17-22 July, 1994.
- Session chair: "Environmental Scanning Electron Microscopy," Scanning '96, Monterey, CA (April 9, 1996).
- Organizer-lecturer: SEM and X-ray Microanalysis Short Course in Singapore (November 4-6, 1996).
- Organizer-lecturer: SEM and X-ray Microanalysis Short Course in Seoul, Korea (March 17-18, 1997).
- Organizer-lecturer: SEM and X-ray Microanalysis Short Course in Bangkok, Thailand (May 19-21, 1997).
- Symposium co-chair: "Nanocrystals and Nanocomposites: Novel Structures for Catalysis, Electronics, and Micromechanics," at the Microscopy & Microanalysis '97 meeting, Cleveland, (Aug. 13, 1997).

Session Co-Chair: "Physical, Chemical, and Biological Properties of Nanometer Particles" for the U.S. Dept. of Energy Workshop: "Instrumentation & Measurement Issues for Nanometer Particles" in Minneapolis (Dec. 5-7, 1997).

Recent Related Invited Presentations

- Invited speaker: "Analysis of Pt-Rh Nanoparticles by X-ray Emission Spectrometry," in Arizona State University High Resolution electron Microscopy Center Winter Workshop, "Materials Science Opportunities for Field Emission Electron Microscopy," Scottsdale, AZ, 5-8 January, 1994.
- Invited speaker: "Quantitative X-ray Microanalysis at Higher Voltages," 52nd annual meeting of the Microscopy Society of America, New Orleans, 31 July – 5 Aug., 1994).
- Invited speaker: "Composition-Size Distribution Diagrams: A New Method for Structure Property Determinations," Workshop on Electron Microscopy of Catalysts - Baltimore (July 5, 1996).
- Invited speaker: "Quantitative Analysis of Metal Nanoparticles," Cleveland, at the Microscopy & Microanalysis '97 meeting (Aug. 11, 1997).
- Invited speaker: "Recent Advances in SEM Techniques," Ford Scientific Laboratory, Dearborn, MI (Oct. 15, 1997).
- Invited Speaker: "Catalytic Alloy Nanoparticles: Structure-Property Relationships" for the U.S. Dept. of Energy Workshop "Instrumentation & Measurement Issues for Nanometer Particles" in Minneapolis (Dec. 5-7, 1997).