New Catalyst Research Instrumentation is Allowing for Quantitative Atomic Composition of the Outermost, Top-Surface Layer of Heterogeneous Catalysts and Sorbents

BY PROFESSOR ISRAEL E. WACHS

The performance of heterogeneous catalysts and sorbents is determined by their surface properties. Detailed knowledge of such surface information can guide the design of advanced catalyst and sorbent materials. The critical surface information about the outermost, top-surface layer of such functional catalysts and sorbents, however, was not accessible with the suite of available characterization techniques. This surface analysis limitation has finally been overcome with the development of high sensitivity–low energy ion scattering spectroscopy that can quantitatively analyze the outermost, top-surface layer of functional solids as well as provide layer by layer composition depth profiling via simultaneous sputtering.

High Sensitivity–Low Energy Ion Scattering Spectrometer

The most advanced high sensitivity–low energy ion scattering (HS-LEIS) spectrometer, the ION-TOF Qtac^{100} HS-LEIS system (**Figure 1**), complete with *in situ* pretreatment chambers (variable gases; T > 1000 °C; P > atmospheric pressure) is the only known characterization technique that quantitatively analyzes the atomic composition of the outermost, top-surface layer of materials (~0.3 nm), such as heterogeneous catalysts and sorbents. Combination of HS-LEIS analysis with simultaneous sputtering also allows for determination of atomic composition information, with trace element detection, for the layers just below the topmost layer. The HS-LEIS spectrometer has recently been acquired by Lehigh University in Bethlehem, PA, the first in North America.

Figure 1. ION-TOF Qtac^{100} HS-LEIS System.

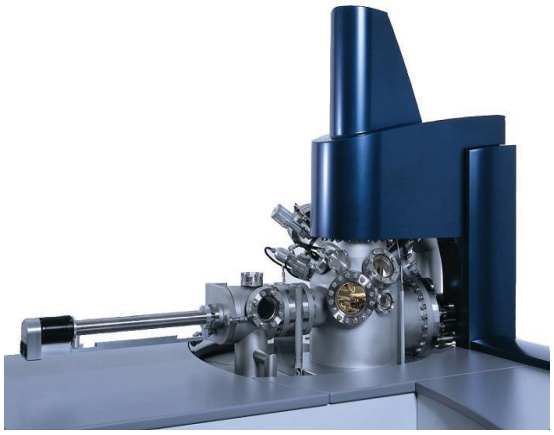
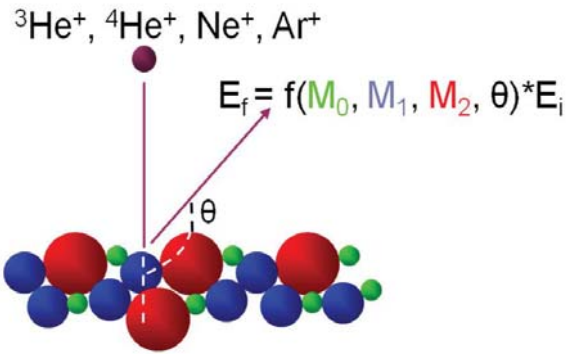
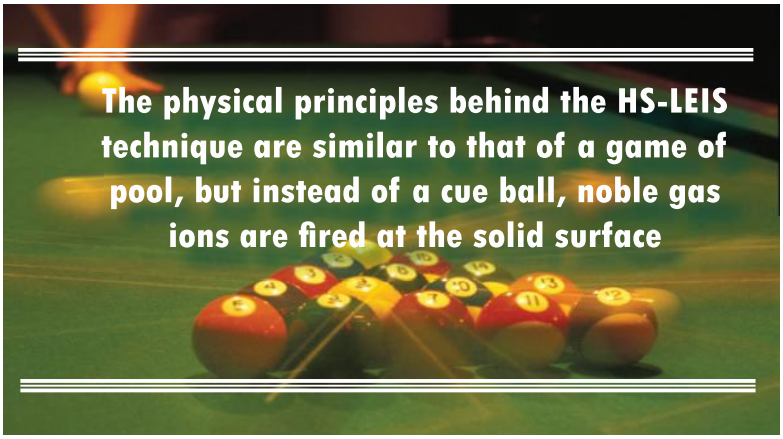


Figure 2. Low energy ion scattering technique principles.



The physical principles behind the HS-LEIS technique are similar to that of a game of pool, but instead of a cue ball, noble gas ions (He^+, Ne^+, Ar^+, Kr^+ or Xe^+) are fired at the solid surface (**Figure 2**). The noble gas ion interacts with a surface atom on the solid surface in a similar way to a cue ball hitting another pool ball: It may either come straight back or be deflected off at some angle, and a fraction of its momentum (or energy) is transferred to the surface atom. The amount of energy lost is directly related to the atomic weight of the surface atom on the solid. It is the energy of the rebounding noble gas ions that is measured in the spectrometer, which can then be related back to unequivocally determine the identity of the atom on the solid surface from which it was scattered.

The unique design of the ION-TOF Qtac^{100} instrument's toroidal energy analyzer to collect scattered ions from all azimuth angles and time-of-flight mass filter to remove secondary ion flux backgrounds at low kinetic energies offers a 3,000 times improvement in sensitivity over its predecessors. Its position sensitive analyzer also allows for two-dimensional surface mapping of the solid surface. The surface compositional information being provided by HS-LEIS is already beginning to change the accepted models for surface composition–property relationships of heterogeneous catalysts. A video presentation by its inventor, Dr. Brongersma, about the theory of HS-LEIS and the type of surface information it can provide is available at www.lehigh.edu/operando.



A recent example of LEIS surface analysis of the composition of the outer layer of bulk mixed molybdate and vanadate catalysts has surprisingly revealed that the surfaces of such bulk mixed metal oxides tend to be reconstructed and enriched with "monolayers" of molybdate and vanadate (Merzlikin and others 2010). Such detailed knowledge about the surface composition of bulk mixed metal oxides has a profound effect on the development of realistic concepts on catalytic active sites, reactant activation, surface reaction mechanisms, and, most importantly, the design of advanced bulk mixed metal oxide catalysts with improved performance for targeted reaction products.

High Resolution X-ray Photoelectron Spectroscopy

Lehigh University is also home to one of the most advanced x-ray photoelectron spectroscopy (XPS) systems with the only Scienta ESCA (electron spectroscopy for chemical analysis)-300 high resolution (HR) x-ray photoelectron system (**Figure 3**) in the western hemisphere for chemical analysis of the surface region (1 to 3 nm). The XPS analyzes the surface region of materials (~1 to 3 nm) and provides quantitative atomic composition, chemical (oxidation) state of elements, bonding information, and valence electronic structures. For example, the HR-XPS readily discriminates between the different Cu oxidation states in Cu–Zn methanol synthesis catalysts after different treatments as shown in **Figure 4**.

The high resolution of the Scienta ESCA-300 HR-XPS arises from the use of high intensity monochromatic x-rays generated from its rotating anode source with a seven-crystal monochromator. The angular resolution of the Scienta ESCA-300 HR-XPS hemispherical analyzer allows for improved surface sensitivity and surface mapping capabilities. The HR-XPS is also equipped with *in situ* pretreatment chambers (variable gases, T > 1000 °C; P > atmospheric pressure). Additional information can be found at http://www.lehigh.edu/~inmicro/esca300.html.

Figure 3. Scieta ESCA-300 high resolution x-ray photoelectron system.

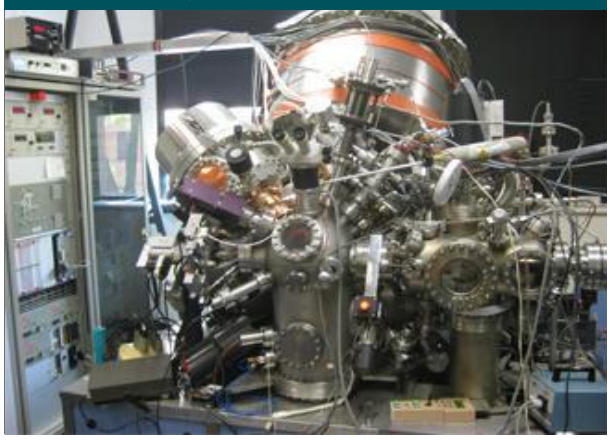
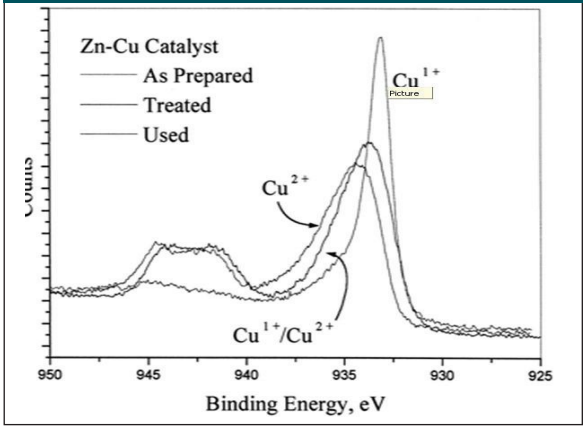


Figure 4. Cu oxidation states in Cu–Zn methanol synthesis catalysts after different treatments.



Conclusion

The combination of cutting edge high sensitivity–low energy ion scattering and HR-XPS surface analysis is now providing critical information about quantitative atomic composition of the outermost, top-surface layer and chemical information about the surface region (oxidation state of elements, bonding information, and valence electronic structures), respectively. These new and unprecedented insights are poised to assist in the design of advanced solid catalyst and sorbent functional materials for targeted applications.

Reference

Merzlikin SV, Tolkachev NN, Briand LE, Strunskus T, Wöll C, Wachs IE, Grünert W. 2010. Anomolous surface compositions of stoichiometric mixed oxide compounds.Angewandte Chemie 47:8037-8041.

Author Biography

Israel E. Wachs is G. Whitney Snyder Professor of Chemical Engineering and Director, *Operando* Molecular Spectroscopy & Catalysis Laboratory, Lehigh University Bethlehem, PA. The current focus of Wachs' catalysis laboratory is to develop catalyst characterization techniques under reaction conditions that will allow establishing structure-activity/selectivity relationships for the molecular design of advanced catalysts for targeted reaction products.

At Lehigh since 1987, he has taught catalysis, energy, environmental and chemical engineering courses and set up a world-class catalysis research laboratory. The research performed by Wachs and his students is well known around the world, as reflected in the many national and international honors from EPA, AIChE, ACS, Fulbright and numerous catalysis societies over the years as well as 16,000+ citations to his 300+ publications (H-Index of ~70).

Previously, Wachs was with Exxon Research & Engineering Company in their Corporate Research Labs (1977 to 1986). He obtained 100 U.S. and international patents during his industrial career, an Exxon Research Incentive Award and was an Exxon Fellow for the spring semester of 1986 at California Institute of Technology (CalTech). He received his undergraduate education at The City College of The City University of New York (1973) and continued his graduate education at Stanford University under the mentorship of Professor Robert J. Madix in the area of surface science of catalysis where he graduated with a PhD (ChE) in 1978. Email:iew0@Lehigh.EDU.

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