Anomalous Surface Compositions of Mixed Oxides

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(PhysOrg.com) -- Mixed oxide compounds are used in many fields including ceramics, catalysis, electrolysis and even pigment design. Despite the extensive applications of such mixed oxide materials, little is known about their outermost surface composition that affects their material and transport properties.

In a recent paper by an international research team from USA, Germany, Russia and Argentina, advanced surface characterization techniques were applied to tease out the elusive outermost surface composition information from several mixed metal oxide systems (Angewandte Chemie *International Edition*, “Anomalous Surface Compositions of Stoichiometric Mixed Oxide Compounds”).

"The new insights reveal that the surfaces of bulk mixed oxides are completely different from what was always believed” said Israel E. Wachs, G.Whitney Snyder professor of chemical engineering at Lehigh University, USA. Other members of the international research team are Wolfgang Grunert, Sergiy Merzlikin, Thomas Strunskus, and Christof Woll of Ruhr-University Bochum, Germany, Nikolay N. Tolkachev of the Russian Academy of Sciences, and Laura E. Briand of the Centro de Investigacion y Desarrollo en Ciencias Aplicadas, Argentina.

The paper examines several bulk mixed oxides such as ZrV_2O_7, $Ce_8Mo_{12}O_{49}$, and α-$Bi_2Mo_3O_{12}$ with Low Energy Ion Scattering (LEIS) spectroscopy and both laboratory-based and synchrotron-based X-ray Photoelectron Spectroscopy (XPS). Using the LEIS sputtering series (destructively removing atomic layer-by-layer with ion bombardment) the authors showed that the mixed oxide compounds contain an outermost monolayer composed of only VO_x or MoO_x of about one atomic layer thickness. After several layers have been sputtered, the bulk composition of the compound is attained.

The authors also note that conventional XPS, from laboratory sources, does not detect this surface enriched metal oxide layer because its depth of analysis is ~1-3 nm, but synchrotron-based XPS is able to detect the anomalous surface layer because of its shallower depth of analysis (~1 nm). The oxide overlayers of bulk mixed oxide compounds are also compared to LEIS sputtering data of supported metal oxide catalysts that possess a surface metal oxide monolayer. The similar trends seen between bulk mixed metal oxides and supported metal oxides hint at the generalization of this phenomenon for all mixed oxide systems, however, the authors also provide and discuss counter-examples.

Aside from discussing surface properties of bulk mixed oxides, the article issues a cautionary statement regarding the discussion of catalytic reaction mechanisms on the basis of surface structures obtained by truncation of the bulk mixed oxide structure, which was the model previously embraced by the scientific community. Furthermore, surface reconstruction during reactions is now an observed and accepted phenomenon, thus, sophisticated surface analysis work is needed to develop realistic reaction mechanisms. Future progress should rely on in situ synchrotron-based XPS and LEIS surface analysis because of their extreme surface sensitivity to ~1.0 nm and ~0.3 nm of the outer surface layer, respectively. "The new insights generated by such precise analysis of the outermost surface layers of mixed metal oxides is poised to establish fundamental structure/composition-function models that will allow for the rational design of advanced materials with tuned surface properties" explains Dr. Wachs.

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