

Measuring the Electronic Structure of Alloy Materials and Relating it to their Catalytic Performance

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Introduction

Identifying structure-performance relationships is critical for the discovery and optimization of heterogeneous catalysts. Recent theoretical contributions have led to the development of d-band theory, relating the electronic structure of metals to their chemical and catalytic activity. While there are many contributions where quantum chemical calculations have been utilized to validate the d-band theory, experimental examples relating the electronic structure of commercially relevant, nonmodel catalysts to their performance are limited. Furthermore, while one can easily predict the d-band center for different metal elements in periodic table, it is not clear what governs the shifts in the d-band center when two or more metals are mixed together to form inter-metallic and alloy compounds.

We have performed electron energy loss spectroscopy (EELS) and Auger electron spectroscopy (AES) studies to show that even small changes in the near Fermi level electronic structure of nonmodel supported catalysts, induced by the formation of surface alloys, can be measured and related to the chemical and catalytic performance of these materials.[4] We demonstrate that critical shifts in the d-band center in alloys are related to the formation of new electronic states in response to alloying, rather than to the charge redistribution among constitutive alloy elements, i.e., the number of d holes and electrons localized on the constitutive alloy elements is constant.

Based on the presented results we provide a simple, physically transparent model for predicting the shifts in the d-band center in response to alloying and relating these shifts to the chemical activity the alloys. While we have performed detailed experimental studies for a family of Ni alloys, we have utilized DFT calculation to test the model for multiple alloys.

Materials and Methods

EELS measurements were carried out in JOEL 2010F field emission electron microscope. The instrument was operated at 200 kV under a pressure of 1.5×10^{-7} torr in scanning transmission electron mode (STEM). AES experiments were conducted using Kratos Axis Ultra XPS with 150W Al (Mono) X-ray gun. This instrument was operated under a pressure of 5×10^{-9} torr. The samples were pre-reduced in a reaction chamber connected to the XPS to avoid oxidation of the samples. The sample were prepared using incipient wetness strategies. The Dacapo pseudo-potentials plane wave code (<http://www.camp.dtu.dk>) was employed for all calculations.

Results and Discussion

EELS and AES were employed to measure the electronic structure of Ni sites on pure monometallic Ni particles and on various Ni alloy particles (mainly Sn/Ni, Au/Ni, and Ag/Ni). These spectroscopic studies showed that there is a measurable change in the Ni electronic structure accompanying the formation of the Ni alloys, see Fig 1(a). The measured change in the electronic structure was related to the formation of new electronic states above

and below the Fermi level. Our experiments also showed that the formation of new electronic states was not accompanied by charge transfer between constitutive alloy elements.

An important consequence of the change in the electronic structure of the Ni sites due to alloying was that the average energy of d-states localized on Ni (the Ni d-band center) was also affected. Through a series of temperature programmed reaction measurements (for example, see Fig 1(b)) we were able to relate the shifts in the d-band center to the chemical activity of the nonmodel alloy catalysts, validating the d-band theory.

Even more importantly, based on the analysis of the factors that govern the shifts in Ni electronic structure to alloying, we have derived a simple and physically transparent model for predicting the shifts in the d-band center in response to alloying and relating these shifts to the chemical activity the alloys. The main feature of the model is that the shift in the position of the d-band center in response to alloying is *only* a function of the width of the band. Since the change in the d-band width in response to alloying is easily predictable, then in principle the shifts in the d-band center and therefore the changes in chemical activity induced by alloying can also be predicted straightforwardly.

While we have performed detailed experimental studies for a family of Ni alloys, DFT calculations were used to test and validate the proposed model for various alloys of different transition and noble metals.

Significance

The presented work validates the d-band theory for supported, nonmodel catalysts. Furthermore, it provides critical insights that allow us to predict the shifts in electronic structure of metals in response to the formation of alloys and to relate these shifts to the chemical activity of alloys.

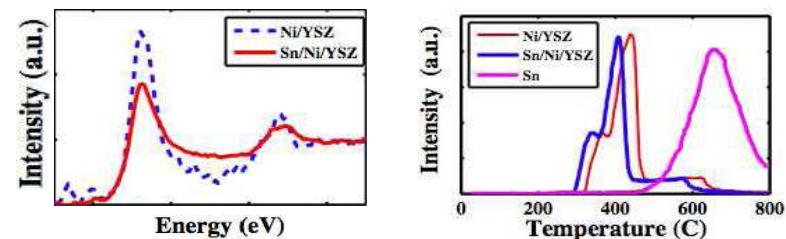


Figure 1. (a) Measured electron loss near edge structure (local density of states projected on Ni above the Fermi level) for Ni atoms in Sn/Ni alloy and monometallic Ni supported on Yttria Stabilized Zirconia (YSZ). (b) Temperature programmed reduction of the Sn/Ni, pure Ni, and pure Sn materials.

References

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