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Operando Characterization of Catalysts through use of a Portable Microreactor

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In order to more deeply understand the mechanisms of catalytic reactions, improved methods are needed to monitor changes that occur in the electronic, structural, and chemical properties of catalytic systems under the conditions in which they work. We describe here a microreactor-based approach that integrates the capabilities of advanced X-ray, electron, optical, and gas-phase compositional analysis techniques under operando conditions. For several exemplary catalytic systems, we demonstrate how this approach enables the characterization of three of the major factors that contribute to structure–property correlations in heterogeneous catalysis. Specifically, we describe how this approach can be used to better understand the atomic structure and elemental composition of nanocatalysts, the physiochemical properties of the support and catalyst/support interfaces, and the gas- and surface-phase chemistry that occurs under operando conditions. We highlight the generality of the approach, as well as opportunities for future developments.

Introduction

In recent years, there has been an acceleration of experimental methods to probe the mechanisms of action that mediate heterogeneously catalyzed chemical reactions. These studies have yielded a more vibrant picture of the dynamic structural complexities that are found in such systems. It is now understood, for example, that structure is a feature of heterogeneous catalysts that is subject to change during the chemical transformations that occur under the high-temperature and pressure conditions at which most catalytic processes operate. The fundamental features of such forms of dynamic, operation-specific transformations are only now beginning to be understood. This highlights an important opportunity for the development of new methods of characterization applicable to the study of heterogeneous catalysts.[1] "Restructuring" commonly refers to the changes that occur in the bonding and composition of a nanocatalyst, and operando-mediated transformations of this type might result in changes in the bonding environments of either near-surface atoms (most common), the catalyst cluster shape, and perhaps most importantly the compositional motif (for example, random alloy to core–shell) of individual metal nanoparticles (NPs).[2] Notably, most heterogeneous catalysts—and even the well-defined model systems used to study them—are not single-phase/elementary composition solids, but rather they are present as a system that comprises distributions of size and composition. This structural heterogeneity can be quite important to the chemistry that the catalytic system supports. In this context, operando forms of restructuring can either lead to or be accompanied by changes in the overall properties of these ensembles, for example, size, shape, and degree of crystalline order.[3] These changes are caused either by: 1) interactions between the metal and the support and/or 2) interactions that result from the catalytic reaction itself, which include the formation, adsorption, desorption, and decomposition of reactants, intermediates, and products. Different experimental techniques have been developed to probe such aspects of heterogeneous catalytic processes, and significant emphasis has been placed on experimental and theoretical methods that address the atomistic underpinnings of the mechanisms of action. Even so, the ability to unify various forms of measurement within a common description of a mechanism remains limited. If we take as an example studies of supported transition-metal nanoscale catalysts, TEM is able

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