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Review

A decade+ of *operando* spectroscopy studies

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ABSTRACT

Because of the ability to directly probe the catalyst under reaction conditions, *operando* studies have significantly improved the catalysis literature. The number of *operando* publications continues to increase. Historical and current *operando* spectroscopy studies concerning all catalyst types and applications are extensively reviewed.

Contents

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1. Introduction: the *operando* spectroscopy methodology

The relationship between catalyst structure, especially surface structure, and reactivity/selectivity remains the most important question in modern heterogeneous catalysis because such fundamental information would allow for rational design of advanced catalysts. It is now well-appreciated that catalyst surfaces are dynamic and are altered by the environmental conditions (T, P, and gas or liquid composition). Consequently, it is critical to establish structure-performance relationships for catalysts operating under relevant reaction conditions given their dynamics.

In situ spectroscopy of heterogeneous catalysts has been practiced for over 60 years and is an invaluable approach for characterizing catalytic materials over a wide range of environmental conditions. *In situ* is Latin for "on site," "on location," or "in position," meaning that catalyst characterization is performed under a controlled atmosphere (vacuum, reducing, oxidizing or reaction conditions) in an environmental cell or chemical reactor. If the treatment or reaction is stopped, and the catalyst is moved to a new location for analysis, then the characterization is referred to as *ex situ*, meaning "off-site" or "from site." The adoption of *in situ* spectroscopy by catalyst scientists since 1965 is shown in Fig. 1. Although its adoption was initially sluggish, the adoption of *in situ* spectroscopy for catalyst characterization started to become rapid during the 1980s and reaching ~480 *in situ* publications in 2015 in the catalysis literature.

In situ characterization studies have allowed scientists to observe catalysts under controlled conditions; however they fall short of providing a direct relationship between catalyst structure (bulk/surface) and performance (activity and selectivity) because of the absence of corresponding reaction product analysis. This is especially true when performed in vacuum or non-reaction conditions (inert (He, Ar, N_2, etc.), O_2 or H_2), as most of such studies tend to be. This limitation of *in situ* spectroscopy characterization, can be overcome by simultaneously collecting catalyst characterization and online product analysis data and has been referred to as *operando* spectroscopy. The term *operando* was coined by Miguel A. Bañares and is Latin for "working" or "operating" and first appeared in the catalysis literature in 2002 from several publications of the Bañares group [1–4]. By simultaneously performing time-resolved *in situ* spectroscopy and online product analysis, it is possible to directly relate the catalyst surface/bulk structure with catalyst performance. The *operando* spectroscopy methodology has been quickly adopted by catalyst scientists since 2002 and