ACS Catalysis

Editorial

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Introduction to Special Issue on Operando and In Situ Studies of Catalysis

This issue features a collection of papers focusing on the emerging area of operando and in situ studies of catalysis, with a significant emphasis on heterogeneous catalysis supplemented with several insightful contributions in homogeneous catalysis. In situ study refers to the real-time investigation of a catalyst, typically by spectroscopy or microscopy techniques, during exposure to reactants or other external stimuli. Recently, scientists and engineers have increasingly applied operando studies of catalysis to directly probe catalysts under working conditions. In operando studies, the catalyst is interrogated via one or more spectroscopy or microscopy techniques under realistic reaction conditions with simultaneous real-time online analysis of reaction products. In some cases, practitioners treat the terms "in situ" and "operando" studies as interchangeable, although the differences delineated above are being increasingly observed.

This special issue includes 25 contributions covering a diverse array of topics in catalysis, including a Review, several Perspectives and Letters, and many Articles.

HETEROGENEOUS CATALYSIS

Unlike molecular catalysis, in which the nature of the catalyst and identity of the active site can be at times straightforward to characterize, heterogeneous catalysis has always been faced with the difficult task of identifying the active site(s) from among a variety of possibilities in a given catalytic material. For this reason, the detailed characterization of the structure of heterogeneous catalysts has always been a cornerstone of heterogeneous catalysis science. In recent decades, practitioners have increasingly turned to in situ characterization of heterogeneous catalysis, and today, operando and in situ studies of catalysis are so widely practiced that an entire subcommunity of operando catalysis scientists is now flourishing. The continued development of advanced spectroscopy and microscopy will undoubtedly continue to drive the growth of the field, and today, many practitioners are combing multiple techniques under operando conditions to probe catalysts in action.

This special issue features a number of papers focused on in situ and operando studies of heterogeneous catalysis. A wide array of catalytic chemistries are covered, ranging from well-established gas phase reactions relevant to commodity chemical and energy production, to selective oxidations of fine chemicals, to electrochemical reactions. A variety of spectroscopy and microscopy techniques are applied, with X-ray absorption spectroscopy (EXAFS and XANES), infrared spectroscopy (DRIFTS, RAIRS, etc.), and X-ray photoelectron spectroscopy (AP-XPS) being most often applied. A number of reports focus on or include application of environmental electron microscopy (TEM, STM) to probe catalysts and catalysis. The collection of papers range from contributions focused on a specific catalyst or technique, to efforts focused on the simultaneous use of multiple techniques under operando conditions, to studies of reacting systems by applying limited in situ or operando studies in targeted ways to help elucidate reaction pathways and mechanisms. Undoubtedly, this diverse collection of contributions speaks to the vibrancy of the field of in situ and operando study of heterogeneous catalysis and provides a nice overview of current activity in the discipline.

HOMOGENEOUS CATALYSIS

Owing to the ease by which regio-, chemo-, and stereoselective control can be tailored and exerted by metal-mediated homogeneous catalysis at low or even ambient temperatures, a multitude of highly selective commercial syntheses of bulk, fine/specialty, and pharmaceutical chemicals have been developed, providing an enormous economic contribution to society. This, in turn, led to many of the first in situ spectroscopic investigations of catalytic reactions. Indeed, one of the pioneers in this area was Dr. Robin Whyman, an industrial scientist at ICI Chemicals, who in the very early 1970s applied in situ infrared techniques to organometallic transformations and, consequently, metal-mediated organic syntheses. This was followed in the 1980s and 1990s by considerable industry-funded academic research.

"Homogeneous Transition-Metal Catalysis: A Gentle Art" is the title of a book by Christopher Masters published in 1980. The title of this book is quite appropriate for the present discussion of in situ studies in homogeneous catalysis, since it hints at both the low temperatures used and the very low activation energy pathways that exist between organometallic species and intermediates in organic synthesis. In part, the widespread use of in situ FTIR and NMR for homogeneous catalytic investigations is directly related to the very low activation energy pathways and, hence, lability of the organometallic transformations. Shorter wavelength radiations can and often do promote side reactions. There appears to be a relatively high awareness in the homogeneous catalytic community that photoinduced reaction pathways are very common under the conditions applied and that the speciation observed when using short-wavelength radiation may be significantly different from the speciation observed when using FTIR and NMR. Therefore, there has been a rather careful and judicious use of both Raman and UV−vis spectroscopies for in situ investigations.

The very detailed molecular information contained in FTIR and NMR measurements has allowed the identification of numerous organometallic intermediates in homogeneously catalyzed syntheses. In turn, this information concerning speciation has allowed researchers to confirm or even correct mechanistic assumptions concerning the primary synthetic pathways. Instrumentation advances have clearly played a dominant role with respect to progress in this field.

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Although appropriate instrumentation is of paramount importance for in situ studies, postprocessing of in situ spectroscopic measurements has significantly increased the utility of such measurements. In the first instance, postprocessing has allowed better signal-to-noise ratios and, hence, improved limits of detection. More importantly, sophisticated deconvolution of the reaction spectra has allowed the generation of accurate pure component spectra. Since spectral overlap is eliminated, ambiguities concerning structural assignments are frequently alleviated. This is particularly true when pure component spectra can be compared with first principal spectral predictions. Finally, since the systems are homogeneous, a further level of postprocessing permits quantitative analysis. Therefore, it is possible to obtain calibrations for all the organometallic and organic species simultaneously and, hence, accurate time-dependent concentrations of both. With the in situ-derived concentrations of intermediates and organics, very detailed kinetic modeling can be performed. At this point, the analysis comes full circle, and the information obtained can be used for rational optimization of the system.

As the preceding paragraph suggests, in situ homogeneous catalytic studies are increasingly multidisciplinary. There is clearly the need for inorganic, organometallic and synthetic chemists on such teams, but it is becoming more apparent that there is also a genuine need and role for engineers, computational chemists, and signal processing experts.

Clearly, in situ studies afford a direct avenue to better understanding of catalysis at a very detailed and fundamental level, but this increased understanding may also influence the next generation of in situ studies in an unexpected manner. Because of the intense interest in intellectual property protection (with respect to new products and new processes) and because of the fact that there are often many ways to generate a particular homogeneous catalytic system, detailed in situ studies may permit new opportunities for the protection of intellectual property.

In conclusion, as a result of the level of fundamental insight being achieved as well as industrial and commercial factors, the future of operando and in situ studies of heterogeneous and homogeneous catalysis looks very bright.

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