ANNALES
UNIVERSITATIS MARIAE CURIE-SKŁODOWSKA
LUBLIN – POLONIA

VOL. LX, 10 SECTIO AA 2005

Operando spectroscopy: new methodology or new name?

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This paper describes bases of the operando methodology. Moreover, indicates similarities as well as differences between classical in situ studies and operando spectroscopy. Infrared in situ studies in catalysis are given as an example that operando methodology was successfully applied in the past under the classical name – in situ studies.

1. INTRODUCTION

In the study of the reacting chemical system, two considerations are of importance. The first is, will the reaction proceed, and if o how far? The second consideration is, how fast does the reaction go, and how quickly is the equilibrium situation attained?

At the beginning of the 19th century it was noticed that a number of chemical reactions were affected by trace amounts of substances (catalysts) that were not consumed in the reaction. The usually accepted definition of a catalyst is that it is a substance that increases the rate at which a chemical system approaches equilibrium, without being consumed in the process [1].

Catalysis plays a key role in nature and society since almost every reaction requires a catalyst or catalytic material [2]. It is possible to divide catalytic systems into two distinct categories: homogeneous catalysis (the catalyst is of the same phase as the reactants and no phase boundary exists) and heterogeneous catalysis (phase boundary separates the catalyst from the reactants). However, there is one important group of substances which cannot be included within this classification, and they are included in a separate category – biocatalysis.

Biocatalysis is essential to all living matter, without it life would not exist. Figure 1 gives an overview of the different catalytic materials presently available [3].

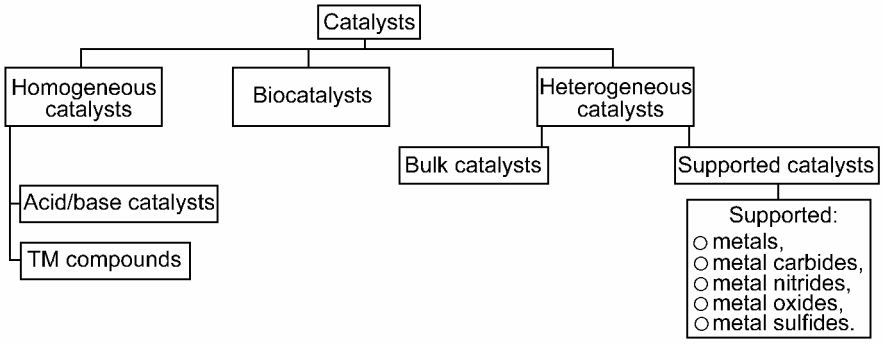

Fig. 1. General overview of catalytic systems (TM – transition metal) [3].

Catalysts facilitate a chemical reaction by lowering the energy barrier of the reaction pathway and thus increasing the reaction rate. Monitoring the events taking place in such materials is crucial for understanding the reaction mechanisms of many important chemical processes and would allow the rational design of new or better catalysts. This monitoring includes the observation of reaction intermediates, the discrimination between spectator species and active sites, the quantification of unusual oxidation states and coordination environments of metal ions in catalyst materials as well as the migration and mobility of species at the catalyst surface [3]. This is the field of in situ spectroscopy where *in situ* refers to the study of catalytic materials at their working place under real reaction conditions [4,5]. Researchers are nowadays working to develop analytical tools that allow them to follow the physicochemical processes taking place in an active catalyst in real time and under operating conditions. These developments have allowed for major advances in catalysis towards the rational design of new and efficient catalysts. The electronic and molecular structures of catalytic active sites and surface intermediates are currently characterized by a large collection of spectroscopic techniques. Sometimes under vacuum conditions with model catalytic systems and in other case under in situ conditions in the presence of chemical probe molecules, reactive environments or reaction conditions [6]. For this purpose the researchers are using in situ characterization techniques to understand the working of catalyst materials [4]. Alternative but also attractive names for this discipline could be in vivo spectroscopy or operando spectroscopy [3]. Operando methodologies appear as an excellent tool to assess the structure-reactivity

relationship at a molecular scale since structural and catalytic parameters are determined simultaneously [3,7-11].

True fundamental understanding of the structure-activity/selectivity relationship requires molecular level characterization of catalytic materials under realistic catalytic operation conditions. The term *in situ* spectroscopy is well established and widely used in the catalysis literature, but *operando* spectroscopic methodology has just recently been introduced into the catalysis literature [3,8] to express a methodology that combines simultaneous *in situ* spectroscopy and kinetic measurements on the same sample and time. *Operando* is borrowed from Latin, which means "working" or "operating" since the spectra are of an "operating" catalyst, whereas, *in situ* means "on site"[3]. The term *in situ* has no temporal discrimination and it is possible to describe several different types of in situ studies [12]:

- *in situ* describes the collection of spectra of a catalytic sample in the same environment were it has been treated or pretreated and the temperature may no longer be that of the pretreatment,
- variable-programmed *in situ* spectra describes the spectra monitor the transformations occurring versus a variable; variable-programmed *in situ* studies may follow the materials under many conditions relevant to catalysis (pressure, temperature, reactant concentration, etc.),
- reaction *in situ* refers to *in situ* spectroscopic measurement under reaction conditions relevant to catalytic operation; in this case, the spectra are taken under conditions relevant to catalytic operation (transient or steady state); to assess if the spectra actually correspond to a catalyst at work, it is possible to use online analysis (e.g., mass spectrometry, chromatography or infrared) to confirm that the catalytic material is actually functioning as a catalyst; however, many *in situ* reactor cell designs may not be appropriate for true catalytic reaction kinetic studies because of complications from gas phase reaction due to large void volumes or heat and mass transfer gradients,
- *operando* methodology describes *in situ* spectra under true catalytic operation as determined by simultaneous online activity/selectivity measurements; the term *operando* provides a single word that underlines the simultaneous evaluation of both structure (catalytic active sites and surface reaction intermediates) and catalytic activity/selectivity.

Various spectroscopic techniques can be applied for *operando* studies. However, among them, Raman spectroscopy is particularly suited for this purpose [12]. Infrared (IR) spectroscopy is complementary to Raman spectroscopy, but IR has some limitations relative to Raman when applied as an *operando* spectroscopy [7]. In some cases IR can be successfully utilized in operando investigations [13-16]. Taking into account the general scheme of IR application in catalysis and

surface science (Fig. 2) it can be seen that in some specific situations this technique was already used for the investigations nowadays named *operando* studies [4].

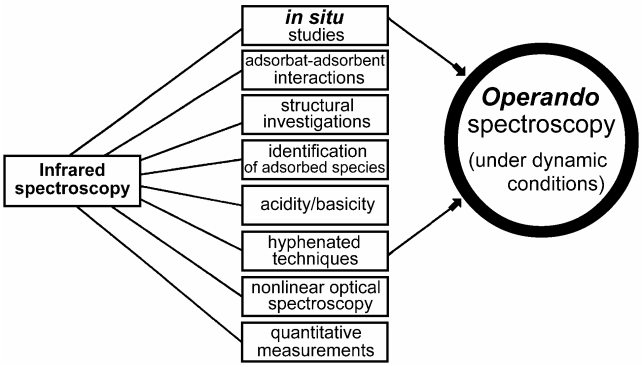

Fig. 2. Proposed application of IR in catalysis.

The combination of *in situ* studies with hyphenated techniques (under dynamic conditions) could describe well the *operando* methodology. A good example of the above is steady-state isotopic transient kinetic analysis (SSITKA) coupled with *in situ* IR [17]. This coupling allowed determination of rate coefficients, elementary rate constants, surface coverages, and residence times of surface intermediates during heterogeneous ethylene hydroformylation over Mn-Rh/SiO_2 catalyst. It is pointed in the quoted literature that recently introduced term *operando* was practically applied almost 30 years ago [12]. In some sense this situation is very similar to those from the beginning of XIX century, when Berzelius "discovered" new power named catalysis.

However, to distinguish classical *in situ* studies from those fitted into *operando* methodology the following scheme can be presented (Fig. 3).

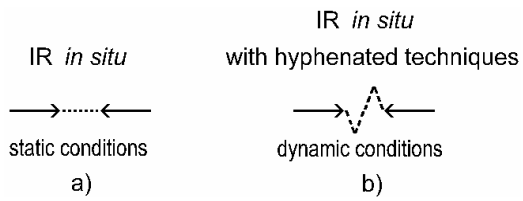

Fig. 3. Schematic presentation of the IR *in situ* studies under static and dynamic conditions: a) classical *in situ* studies, b) *operando* spectroscopy.

Splitting *in situ* studies for the two general categories has an additional advantage (beside the methodological one) [18]. Adapting newly introduced and accepted in the scientific community terminology, instead of telling/writing: IR *in situ* studies with hyphenated techniques under dynamic conditions, someone can use more condensed description: IR *operando* spectroscopy.

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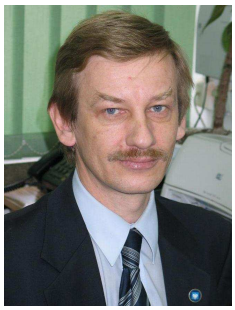

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