Available online at www.sciencedirect.com
SCIENCE DIRECT®

Catalysis Today 100 (2005) 71–77

CATALYSIS TODAY

www.elsevier.com/locate/cattod

Operando methodology: combination of in situ spectroscopy and simultaneous activity measurements under catalytic reaction conditions

Miguel A. Bañares *

Instituto de Catálisis y Petroleoquímica, CSIC, Marie Curie 2, E-28049 Madrid, Spain

Abstract

Operando spectroscopy is a methodology that combines the spectroscopic characterization of a catalytic material during reaction with the simultaneous measurement of catalytic activity/selectivity. *Operando* spectroscopy is a new term that has been introduced into the catalysis literature at the beginning of the 21st century that underlines the importance of *simultaneously* combining fundamental spectroscopic surface phenomenon with catalytic performance, *on the same sample*, under realistic reaction conditions. The potential impact of *operando* spectroscopy on catalysis science lies in its ability to significantly assist in the establishment of fundamental molecular structure–activity/selectivity relationships for catalytic systems. It is critical that the design of the spectroscopic reaction cell, the catalytic reactor, also allows for the generation of catalytic performance data that is analogous to those achieved with conventional catalytic reactors. A case study of *operando* Raman-GC study is presented along with consideration of the methodology, spectroscopy and samples.

Keywords: Spectroscopy; Raman; *Operando*; In situ; Catalyst; Synthesis; V-Sb-O; Antimonate; Vanadium oxide; Antimony oxide; Propane; Ammoxidation; Acrylonotrile; Propylene

1. *Operando* catalytic spectroscopy

Heterogeneous catalysts play a key role in chemical industry since most products are produced by catalytic processes. Understanding the structure–activity relationships at the molecular and atomic scale is of significant importance in assisting the improvement of existing catalytic processes as well as developing new catalytic processes. In situ spectroscopic studies have significantly advanced catalysis science by providing fundamental information about catalytic structure and surface species under controlled environments [1–22]. These developments have allowed for major advances in catalysis science 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 cases under in situ conditions in the presence of chemical probe molecules, reactive environments (reduction, oxidation, etc.) or reaction conditions. These different scenarios provide fundamental information about the electronic and molecular structures of the catalytic active sites and surface intermediates. The surface state of a catalyst is strongly affected by the environmental conditions (pressure, temperature, reactants, products, etc.). Under typical catalytic reaction conditions, the reactants concentrate on the solid surface [4,5] and induce changes in the surface structure. A comparison of the surface of Rh and Pt in vacuum and at nearly atmospheric pressure by infrared–visible sum frequency generation with simultaneous online gas chromatographic analysis of the gas phase, an *operando* investigation, clearly illustrates the reconstruction of the surface during catalytic operation that is not observed under vacuum conditions [4]. Exposure of the heterogeneous catalyst to adsorbates has been shown to reconstruct many catalytic surfaces [2,5,15–17]. Many surface reaction

---

* Tel.: +34 915854788; fax: +34 915854760.
E-mail address: mbanares@icp.csic.es

0920-5861/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2004.12.017

intermediates may also not be present far from reaction conditions (e.g., vacuum). It is also important to underline that a number of industrial catalytic systems undergo transient activation or deactivation processes, which may also be related to surface structural changes. These pressure and material ''gaps'' must be bridged for the development of structure–activity relationships [1–22]. Thus, unfortunately, confusion may arise from attempts to correlate the structure of a catalyst at conditions that are not relevant to its catalytic operation (e.g., ambient conditions where the surfaces are hydrated with moisture and their structures are different than those under reaction conditions) [12–14,23–35].

Fundamental structure–activity/selectivity relationships are critical for the development of knowledge-based design of new and novel catalytic materials for different applications. True fundamental understanding of the structure–activity/selectivity relationship requires molecular level characterization of catalytic materials under realistic catalytic operation conditions [2,3,5,23]. I would now like briefly digress from catalysis science to etymology. 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 in 2002 [24,25,34] to express a methodology that combines simultaneous in situ spectroscopy and kinetic measurements on the same sample and time. The details of this Latin term are described elsewhere [23]. ''*Operando* is borrowed from Latin'', which means ''working'' or ''operating'' since the spectra are of an ''operating'' catalyst, whereas, ''in situ'' means ''on site''. Etymologically, the term in situ has no temporal discrimination and it is possible to describe several different types of in situ studies:

(a) ''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.

(b) Variable-programmed ''in situ'' spectra describes the spectra monitor the transformations occurring versus a variable. For instance, during a temperature-programmed process such as TPR-Raman for the reduction of a sample [26–28], TPO-Raman [26,29] during for oxidation of a sample, or TPSR-Raman to investigate the surface reactions of adsorbates of chemical probe molecules [30]. Or in general, any transformation that may occur during heating [31,32]. The in situ temperature-programmed Raman (TP-Raman) studies follow the evolution of a sample under controlled atmosphere versus temperature. Variable-programmed in situ studies may follow the materials under many conditions relevant to catalysis (pressure, temperature, reactant concentration, etc.) [33].

(c) ''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.

(d) ''*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 [23–25,34,35].

Among all the available spectroscopic techniques, Raman spectroscopy is particularly suited for in situ studies since there is negligible interference from the gas phase due to the weak light scattering from the low density of molecules in the gas or vapor phase. The Raman spectra may be acquired over a wide range of sample temperature (from at least liquid He and N_2 to 1300 °C) [36,37] and pressure (vacuum to several atmospheres). Visible excitation (typically, from 488 to 633 nm) is mostly employed and the convenient optical arrangements of current Raman systems allow for the design of environmental catalytic reactor cells that perform similarly to conventional catalytic reactors during the *operando* spectroscopic studies. Therefore, Raman spectra can be collected during catalytic operation to provide molecular level insight into the structure–activity/selectivity relationships of catalytic active sites and the associated surface intermediates when present.

The activity/selectivity measurement method (e.g., GC, MS, IR, etc.) should also be contained in the *operando* spectroscopy nomenclature. For example, Raman spectra acquired during catalytic operation with simultaneous online gas-chromatograph activity measurement should be referred to as ''*operando* Raman-GC''. *Operando* spectroscopy may also find application in other technological fields where environmental (temperature, pressure and atmosphere) spectroscopy will provide fundamental information about the molecular structure and performance of various the materials. It needs to be further emphasized that ''*operando*'' means an action, whereas, ''in situ'' means at a location and, consequently, it is grammatically incorrect to say ''in *operando*''.

A growing number of papers have appeared in the catalysis literature using the term ''*operando*'' since it was first proposed in 2002 [24,25,34,35]. The ISI Web of Science has 18 entries for papers employing this term, 16 of the papers are actually using *operando* spectroscopic techniques [24,25,34,35,38–51]. Several conferences have already been organized on *operando* spectroscopy [52–56]. *Operando* expresses a concept that has previously been employed by several catalysis researchers. Most of the available in situ catalyst spectroscopic techniques have already been used in the *operando* mode. It appears that the earliest *operando* paper is that reported by Tamaru combining pulses of reactants to an infrared cell containing catalysts with simultaneous chromatographic analyses of the products [57]. Possibly the earliest *operando* Raman study was reported by Hill et al. [58]. Several researchers have already also reported reaction in situ studies with simultaneous evaluation of activity for other spectroscopic techniques: SFG-MS [5], EPR-GC [59], XRD [60] or NMR [61]. There is now clearly a trend in the catalysis literature on the progress of several in situ spectroscopic characterization techniques with increasing emphasis on catalytic reaction conditions. An issue devoted to in situ characterization of catalysts has recently appeared in *Topics in Catalysis*, edited by Thomas and Somorjai [62]. On occasion of this 100th issue of *Catalysis Today*, it is interesting that one of the earliest journal issues devoted to in situ spectroscopy under reaction conditions was published in a special issue of *Catalysis Today* edited by Burch [19]. That issue is a milestone for the combination of in situ spectroscopy and kinetic analyses in catalytic science and even includes several *operando* papers, however, before the *operando* word appeared in the catalysis literature: *operando* DRIFTS-MS [63], *operando* thermography-IR product analyzer and concentration-programmed experiment [33], *operando* IR-GC [64], *operando* IR-mass spectrometry [65], *operando* electrochemistry-chromatography [66], and *operando* EXAFS-chromatography [67,68].

2. Considerations about *operando* experiments

Operando studies provide molecular level information about the dynamic states of catalytic active sites and about the surface reaction intermediates during catalytic reactions, with both structure and activity being simultaneously determined. In addition, the catalytic *activity data* determined in the *operando* reactor cell should also agree with the corresponding results from conventional reactors. Such data are presented in Table 1 where conversion and selectivity values for an alumina-supported molybdena-vanadia catalyst during propane oxidative-dehydrogenation reaction are compared in a conventional fixed-bed reactor and in an *operando* fixed-bed reactor cell [41]. The excellent agreement for the results from both reactor types demonstrates that this is indeed a realistic goal for *operando* spectroscopy studies. Such considerations had previously also been achieved by other groups that combined in situ spectroscopy and online activity/selectivity measurements [60,69–73].

Table 1
Conversion and selectivity values of a Mo–V–O/γ-Al_2O_3 catalyst in conventional and *operando* fixed-bed reactors

Reactor	Temperature (°C)	Conversion (mol%)	Selectivity		
			Propylene	CO	CO_2
Conventional	320	5.7	49.5	31.2	19.3
Operando	320	5.6	45.6	35.6	18.8

Reaction conditions: catalyst weight, 300 mg, total flow 90 ml/min, C_3H_8/O_2/He = 1/12/8 mol.

In addition, the selection of the specific catalytic reaction system and the spectroscopic technique will also have a major impact on the relevance of the electronic and molecular structure information that can be obtained with *operando* spectroscopy investigations. Supported oxide catalysts are particularly suited for such studies since the catalytic active sites are generally 100% dispersed on the oxide support surface and, therefore, directly exposed to the reaction environment. Raman spectroscopy is particularly suited to study supported oxides since most oxides employed as support materials are not Raman active (Al_2O_3), give rise to only very weak Raman bands (SiO_2) or do not exhibit intense Raman bands above 700 cm^{-1} (e.g., ZrO_2, TiO_2, Nb_2O_5, Ta_2O_5, SnO_2, Fe_2O_3, etc.) that can interfere with the most informative Raman modes for the supported oxide catalysts [7–17,34,74]. Thus, the Raman information about the supported metal oxide is directly relevant to the catalytic reaction.

Bulk oxides possess a three-dimensional character, and most typically, only the outermost layer is exposed to the reacting molecules. Most spectroscopic characterization techniques, including Raman, able to function under reaction conditions only provide information about the bulk structures and are *not* surface spectroscopic techniques. Consequently, the spectroscopic signals will be dominated by the contribution from the oxide bulk rather than the outermost surface. Furthermore, bulk electronic and molecular structures are not expected to directly correlate with the catalytic performance taking place on the outermost surface layer. Nevertheless, the reaction environment may simultaneous modify both the bulk lattice and the surface layer of the catalyst [75]. For instance, V-P-O catalysts undergo significant changes in performance and in situ spectroscopic studies underline the bulk lattice re-structuring of this system during n-butane oxidation to maleic anhydride [76–82] as well as crystallization of the outermost layers with reaction time [77]. These bulk and surface structural transformations have been correlated with the V-P-O catalytic performance and occur because the redox catalytic cycles and the water product generated [75–82]. It is interesting to note that the catalytic performance of surface VO_x and PO_x dispersed on a titania support is actually similar to that of bulk V-P-O during butane oxidation [83]. This observation suggests that highly dispersed supported metal oxide catalytic systems are probably excellent models for the corresponding bulk mixed metal oxide systems. Interestingly, several recent investigations are beginning to reveal that the surface composition of many mixed metal oxide catalytic systems may also be very different than the bulk lattice composition [77,84–87]. In some cases, the surfaces of bulk mixed metal oxides have even been found to be decorated by a complete close-packed monolayer of only one of the metal oxide components [88–90]. These recent findings have enormous implications for the catalysis science of mixed metal oxide catalysts.

For most bulk mixed metal oxide systems, the surface-to-volume ratio is rather low because of their generally modest surface areas (Fig. 1). This low number of surface sites and their weak spectroscopic signals accounts for why the spectra of mixed metal oxides are dominated by the bulk metal oxide phases. One approach to minimize this limitation is to minimize the particle size of the mixed metal oxides by supporting such catalytic materials on a high surface area support. Thus, the surface-to-volume ratio for such systems is significantly increased and the spectroscopic analysis of the outermost surface layer is significantly facilitated. In addition, this also allows for the stabilization of nano-sized crystallites on an oxide support without the typical sintering that is observed for the corresponding unsupported mixed metal oxide catalysts [91–93] (see Fig. 1).

3. *Operando* Raman-GC case study

The structural and kinetic behavior of an alumina-supported nanocrystalline vanadium antimonate mixed oxide catalytic system during propane ammoxidation is presented in Fig. 2 [25,42]. The left side of the figure shows the Raman spectra for the alumina supported mixed Sb–V–O oxides under different reaction environments, and the right hand side of the figure contains the corresponding catalytic activity/selectivity data. Total loading of the supported VO_x and SbO_x metal oxides was chosen to be close to monolayer surface coverage. The catalyst was found to activate during time on stream under the propane ammoxidation reaction in a conventional fixed bed reactor at a given temperature [92], which is in line with literature data. The in situ Raman spectra of the dehydrated fresh and used catalyst underline the important modifications in the molecular structures of the supported Sb–V–O catalyst during the propane ammoxidation reaction [92]. The fresh catalyst in the *operando* cell at 200 °C exhibits Raman features $\sim$1024 cm^{-1} (corresponding to the terminal V=O stretching vibration) and a broad Raman band centered at $\sim$900 cm^{-1} (associated with the stretching vibration of the bridging V–O–V bond) that are characteristic of surface vanadia species on alumina under dehydrated conditions. No features of antimony oxide are evident due to the weak signal from the amorphous Sb oxide species on alumina. As the reaction temperature increases, catalytic activity becomes measurable and the Raman spectra of the catalyst undergo significant transformations. For example, the vibrational mode at 1024 cm^{-1} belonging to the surface VO_x species on Al_2O_3 almost disappears and the broad band centered at $\sim$900 cm^{-1} shifts to a new broad band centered at $\sim$800 cm^{-1}, which is characteristic of crystalline $VSbO_4$ (rutile). In addition, new Raman bands at 190 and 250 cm^{-1} also appear that are characteristic of characteristic of crystalline Sb_2O_4. The new crystalline metal oxide phases form at the expense of the surface SbO_x and VO_x species. At 480 °C, the catalyst possesses nano-crystalline $SbVO_4$ and Sb_2O_4 phases and also becomes more selective towards acrylonitrile formation. The catalytic activity/selectivity values in the *operando* spectroscopic reactor are in agreement with those obtained in the conventional fixed bed reactor [92,25]. Bulk Sb_2O_4 is a mixed-valence oxide containing both Sb^{3+} and Sb^{5+} sites. The oxidation states in crystalline bulk $SbVO_4$ are Sb^{5+} and V^{3+} according to Mössbauer and EPR spectroscopy, respectively [94,95]. An *operando* EPR study also confirmed the formation of V^{3+} species in the corresponding titania-supported V-Sb-O catalytic system [43]. This *operando* Raman-GC case study nicely demonstrates the potential of the *operando* methodology to follow the genesis of the active catalyst under reaction conditions and, thus, directly establish links between catalyst structure and activity/selectivity during reaction conditions.

Reoxidation does not affect the crystalline bulk $VSbO_4$ phase, but restores some of the surface vanadia V^{5+} species (Raman band at 1024 cm^{-1}) and decreases the signal from the segregated crystalline bulk Sb_2O_4 phase. These structural changes are reversible since upon returning to the ammoxidation reaction conditions the surface VO_x Raman signal is significantly diminished and the crystalline Sb_2O_4 Raman signal is again enhanced. Bulk $VSbO_4$ appears to facilitate these structural transformations since it is able to form many stoichiometries around the $V_1Sb_1O_4$ structure [96,97]. Accordingly, incorporation of V^{3+} into $VSbO_4$ results in higher amounts of segregated α-Sb_2O_4 and vice versa. The reversible migration of V cations from the $VSbO_4$ lattice appears to be compensated by the migration

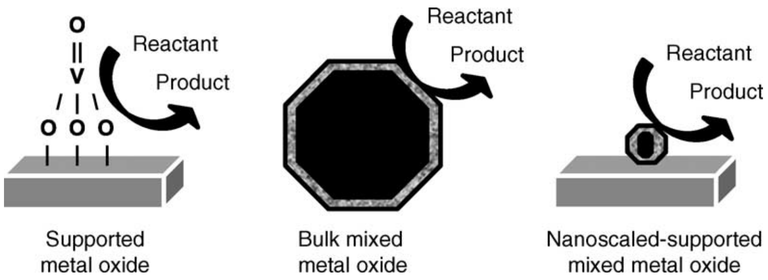

Fig. 1. Schematic of supported metal oxide catalyst (left), bulk mixed oxide catalyst (center) and model supported nano mixed oxide catalyst (right).

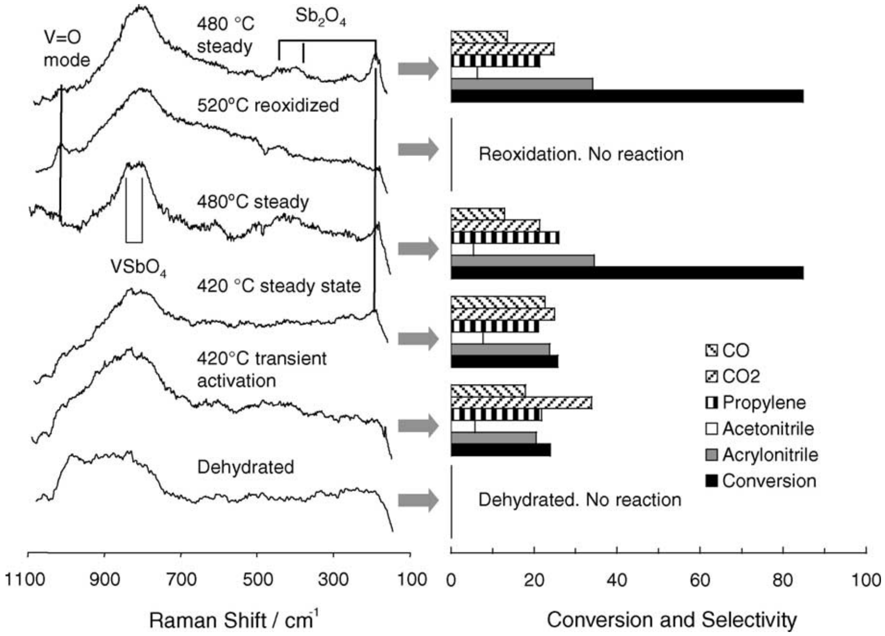

Fig. 2. Raman spectra and activity data during propane ammoxidation in the *operando* fixed-bed reactor with 200 mg of alumina; supported Sb–V–O mixed oxides at monolayer coverage (16.7 wt.% Sb + 7.0 wt.% V), atomic ratio Sb/V = 1; W = 200 mg, total flow, 20 ml/min, 25% O_2 + 9.8% C_3H_8 + 8.6% NH_3 in He (adapted from M.O. Guerrero-Pérez, M.A. Bañares, Catal. Today 78 (2004) 265).

of Sb^{5+} cations [42]. Vanadium sites in Sb–V–O/Al_2O_3 system undergo a redox cycle involving surface vanadium oxide species concomitant to transformation of the segregated antimony oxide [25,42].

The above example nicely demonstrates the capabilities of *operando* Raman-GC, but each spectroscopic technique provides a piece of electronic and molecular structural information of the catalytic materials and the influence of the catalytic reaction environments. A detailed understanding will typically require the concurrence of several complementary spectroscopic techniques [43]. For instance, the presence of reduced oxidation states of supported oxides during reaction cannot always be clearly established with Raman spectroscopy measurements. Combination of UV–vis-DRS and Raman spectroscopy, however, provide better understanding of oxidation states of supported vanadium oxide catalysts at different surface coverage, on different oxide supports and with different hydrocarbons [98–102]. Combined Raman and UV–vis-DRS also allows for correction of Raman signal intensity as well as information on the oxidation states of supported oxide catalysts during non-oxidative dehydrogenation conditions [8,103]. The combined use of IR and Raman also provides information about the nature of chemisorbed species and the catalytic active sites during reaction conditions [102,104] and under *operando* conditions [30]. Thus, the combined use of several complementary techniques affords more detailed electronic and molecular structural insights into the nature of surface catalytic active sites as well as surface reaction intermediates and their adsorption sites on the catalyst.

4. Conclusions

The *operando* methodology is a combined spectroscopic measurement and *simultaneous* online measurement of catalytic activity/selectivity values during catalytic reaction studies. The contemporary catalyst structural and kinetic data greatly facilitates the molecular level understanding of the structure–activity/selectivity relationships of catalytic materials under different reaction conditions. Both the catalyst structure and activity/selectivty must be relevant to the catalytic system being investigated. The optimum spectroscopic cell for *operando* studies should be designed to provide catalytic performance data similar to a conventional catalytic reactor. The catalytic material and spectroscopic techniques should be chosen so that the structural information obtained is relevant to the realistic catalytic reaction condition. The use of several spectroscopic techniques will provide complementary information that will significantly contribute to the molecular and atomic understanding of structure–activity/selectivity relationships.

Acknowledgements

This research is partly funded by the Spanish Ministerio de Educación y Ciencia (MAT-2002-0400-C02-01) and by the COST Action D15/0021/01 under ESF. This article is dedicated to Dr. M.V. Martínez-Huerta, Dr. M.O. Guerrero-Pérez and Ms. S.J. Khatib, whose efforts contribute to the extension of in situ to *operando* studies.

References

[1] J.M. Thomas, Recent trends in surface science and their impact on catalyst characterization, in: J.M. Thomas, R.M. Lambert (Eds.), Characterization of Catalysts, Wiley, 1980.
[2] H. Topsøe, Stud. Surf. Sci. Catal. 130 (2000) 1.
[3] J.M. Thomas, G.A. Somorjai, Preface, catalyst characterization under reaction conditions, Topics Catal. 8 (1–2) (1999).
[4] G.A. Somorjai, G. Rupprechter, J. Phys. Chem. B 103 (1999) 1623.
[5] F. Zaera, Prog. Surf. Sci. 69 (2001) 1.
[6] J.M. Thomas, Angew. Chem. Int. Ed. 38 (1999) 2588.
[7] P. Stair, Curr. Opin. Solid State Mater. Sci. 5 (2001) 365.
[8] S. Kuba, H. Knözinger, J. Raman Spectrosc. 33 (2002) 325.
[9] G. Mestl, J. Mol. Catal. A 158 (2000) 45.
[10] H. Knözinger, G. Mestl, Topics Catal. 8 (1999) 45.
[11] H. Knözinger, Catal. Today 32 (1996) 71.
[12] I.E. Wachs, Topics Catal. 8 (1999) 57.
[13] I.E. Wachs, Surf. Sci. 544 (2003) 1.
[14] I.E. Wachs, Raman spectrsocopy of catalyts, in: I.R. Lewis (Ed.), Handbook of Raman Spectrsocopy, Marcel Dekker, NY.
[15] G.A. Somorjai, Chem. Rev. 96 (1996) 1223.
[16] H.E. Shih, F. Jona, P.M. Marcus, Phys. Rev. Lett. 46 (1981) 731.
[17] Y. Gauthier, R. Baudoing-Savois, K. Heinz, H. Landskron, Surf. Sci. 251 (1991) 493.
[18] J.A. Dumesic, H. Topsøe, Adv. Catal. 26 (1977) 121.
[19] R. Burch (Ed.), In situ methods in catalysis, Catal. Today 9 (1–2) (1991).
[20] J.W. Niemansverdriet, Spectroscopy in Catalysis, VCH, 1993.
[21] B.S. Clausen, H. Topsøe, R. Frahm, Adv. Catal. 42 (1998) 315.
[22] G.A. Somorjai, Cattech 3 (1999) 84.
[23] B.M. Weckhuysen, Chem. Commun. (2002) 97, feature article in ref. 11.
[24] M.A. Bañares, M.O. Guerrero-Perez, J.L.G. Fierro, G.G. Cortez, J. Mater. Chem. 12 (2002) 3337.
[25] M.O. Guerrero-Perez, M.A. Bañares, Chem. Commun. (2002) 1292.
[26] M.A. Bañares, J.H. Cardoso, F. Agulló-Rueda, J.M. Correa-Bueno, J.L.G. Fierro, Catal. Lett. 64 (2000) 191.
[27] J.M. Kanervo, M.E. Harlin, A.O.I. Krause, M.A. Bañares, Catal. Today 78 (2003).
[28] T. Montini, M.A. Bañares, N. Hickey, R. Di Monte, P. Fornasiero, J. Kaspar, M. Graziai, Phys. Chem. Chem. Phys. 6 (2004) 1.
[29] J.E. Herrera, D.E. Resasco, Chem. Phys. Lett. 376 (2003) 302.
[30] L.J. Burcham, G. Deo, X. Gao, I.E. Wachs, Topics Catal. 11/12 (2000) 85.
[31] C.L. Pieck, M.A. Bañares, M.A. Vicente, J.L.G. Fierro, Chem. Mater. 13 (2001) 1174.
[32] G.I.N. Waterhouse, G.A. Bowmaker, J.B. Metson, Appl. Surf. Sci. 214 (2003) 36.
[33] J. Kellow, E.E. Wolf, Catal. Today 9 (1991) 47.
[34] M.A. Bañares, I.E. Wachs, J. Raman Spectrosc. 33 (2002) 359.
[35] G. García-Cortéz, M.A. Bañares, J. Catal. 209 (2002) 197.
[36] V.V. Pushkarev, V.I. Kovalchuk, J. D'Itri, J. Phys. Chem. B 108 (2004) 5341.
[37] X. Wang, I.E. Wachs, Catalysis by metal oxides: comparison between bulk mixed oxides, supported oxides, oxide clusters, organometallic oxides and oxide single crystals, in: Proceedings of the Symposium at the 228th ACS Meeting, Philadelphia, 22–26 August 2004.
[38] E. Odier, Y. Schuurman, K. Barral, C. Mirodatos, Stud. Surf. Sci. Catal. 147 (2004) 79.
[39] B. Coq, G. Delahay, R. Durand, D. Berthomieu, E. Ayala-Villagomez, J. Phys. Chem. B 108 (2004) 11062.
[40] T. Lesage, C. Verrier, P. Bazin, J. Saussey, S. Malo, C. Hedouin, G. Blanchard, M. Daturi, Topics Catal. 30–31 (2004) 31.
[41] M.A. Bañares, S.J. Khatib, Catal. Today 96 (2004) 251.
[42] M.O. Guerrero-Pérez, M.A. Bañares, Catal. Today 96 (2004) 265.
[43] U. Bentrup, A. Brückner, C. Rudinger, H.J. Eberle, Appl. Catal. A 269 (2004) 237.
[44] G. Mul, G.M. Hamminga, J.A. Moulijn, Vib. Spectrosc. 34 (2004) 109.
[45] M.H. Groothaert, K. Lievens, H. Leeman, B.M. Weckhuysen, R.A. Schoonheydt, J. Catal. 220 (2003) 500.
[46] T.A. Nijhuis, S.J. Tinnemans, T. Visser, B.M. Weckhuysen, Phys. Chem. Chem. Phys. 5 (2003) 4361.
[47] G. Mul, M.A. Bañares, G.G. Cortez, B. vd Linden, S.J. Khatib, J.A. Moulijn, Phys. Chem. Chem. Phys. 5 (2003) 4378.
[48] O. Demoulin, M. Navez, E.M. Gaigneaux, P. Ruiz, A.S. Mamede, P. Granger, E. Payen, Phys. Chem. Chem. Phys. 5 (2003) 4394.
[49] T. Lesage, C. Verrier, P. Bazin, J. Saussey, M. Daturi, Phys. Chem. Chem. Phys. 5 (2003) 4435.
[50] A. Brückner, Phys. Chem. Chem. Phys. 5 (2003) 4461.
[51] C. Lamberti, S. Bordiga, F. Bonino, C. Prestipino, G. Berlier, L. Capello, F. D'Acapito, F.X.L.I. Xamena, A. Zecchina, Phys. Chem. Chem. Phys. 5 (2003) 4502.
[52] The first Operando Congress was celebrated in Lunteren, Netherlands, 2–6 March 2003. Organized by B.M. Weckhuysen, M.A. Bañares, E. Gaugneaux, P. Van Der Voort, G. Mestl (http://www.icp.csic.es/operando).
[53] Several reports on the Operando-I meeting can be found in: I.E. Wachs, Catal. Commun. 4 (2003) 567; I.E. Wachs, Cattech 7 (4) (2003) 142.
[54] The Second Operando Congress will be celebrated in Toledo, Spain, 23–27 April 2006. Organized by M.A. Bañares, F. Thibault-Starzyk, A. Brückner, E. Gaigneaux, B.M. Weckhuysen (http://www.berlin-aca.de/operando).
[55] A course on in situ and operando spectroscopy for catalysis was organized at Caen, France, 18–21 July 2004, by C. Fernandez and M. Daturi.
[56] There is a special session about Operando spectrsocopy chaired by I.E. Wachs, in the 19th North American Catalysis Society Meeting, Philadelphia, USA, 22–27 May 2005 (http://www.19nam.org).
[57] T. Okawa, T. Onishi, K. Tamaru, Zeitschrift für Physikalische CEIME-Frankfurtr 107 (1977) 239.
[58] J.H. Wilson, C.G. Hill, J.A. Dumesic, J. Mol. Catal. 61 (1990) 333.
[59] P. Rybaczyk, H. Berndt, J. Radnik, M.M. Pohl, O. Buyevskaya, M. Baerns, A. Brückner, J. Catal. 202 (2001) 45.
[60] B.S. Clausen, G. Steffensen, B. Fabius, J. Villadsen, R. Feidenhans'l, H. Topsøe, J. Catal. 132 (1991) 189.
[61] M. Hunger, Catal. Today 97 (2004) 3.
[62] In situ characterization of catalysts under reaction conditions, in: J.M. Thomas, G.A. Somorjai (Eds.), Topics in Catalysis, vol. 8, 1999.
[63] J.G. Highfield, M. Prairie, A. Renken, Catal. Today 9 (1991) 39.
[64] M.A. Makarova, E.A. Paukshtis, J.M. Thomas, C. Williams, K.I. Zamaraev, Catal. Today 9 (1991) 61.
[65] N.Y. Topsøe, H. Topsøe, Catal. Today 9 (1991) 77.
[66] H.H. Hildenbrand, H.G. Linztz, Catal. Today 9 (1991) 153.
[67] S. Clausen, H. Topsøe, Catal. Today 9 (1991) 189.
[68] E.A. Shaw, T. Rayment, A.P. Walker, R.M. Lambert, T. Gauntlett, R.J. Oldman, A. Dent, Catal. Today 9 (1991) 197.
[69] T.P. Snyder, C.G. Hill, J. Catal. 132 (1991) 536.
[70] B.S. Clausen, G. Steffensen, B. Fabius, J. Villadsen, R. Feidenhans'l, H. Topsøe, J. Catal. 132 (1991) 524.
[71] G. Mestl, Raman J. Spectrosc. 33 (2002) 333.
[72] M.A. Bañares, L. Dauphin, X.J. Lei, W. Cen, M.Y. Shang, E.E. Wolf, T.P. Fehlner, Chem. Mater. 7 (1995) 553;
M.A. Bañares, L. Dauphin, V. Calvo-Perez, T.P. Fehlner, E.E. Wolf, J. Catal. 152 (1995) 396.
[73] S.B. Xie, M.P. Rosynek, J.H. Lunsford, Appl. Spectrosc. 53 (1999) 1183.
[74] I.E. Wachs (Ed.), Characterization of Catalytic Materials, Butterworth-Heinemann, Manning, Greenwich, CT, 1992.
[75] G.J. Hutchings, A. Desmartinchomel, R. Olier, J.C. Volta, Nature 368 (1994) 41.

[76] V.V. Guliants, S. Holmes, J.B. Benziger, P. Heaney, D. Yates, I.E. Wachs, J. Mol. Catal. A 172 (2001) 265.
[77] V.V. Guliants, J.B. Benziger, S. Sundaresan, N. Yao, I.E. Wachs, Catal. Lett. 32 (1995) 379.
[78] F.B. Abdelouahab, R. Olier, N. guilhaume, F. Lefebvre, J.C. Volta, J. Catal. 134 (1992) 151.
[79] F.B. Abdelouahab, R. Olier, N. guilhaume, F. Lefebvre, J.C. Volta, ACS Symp. Ser. 523 (1992) 217.
[80] G. Koyano, T. Saito, M. Misono, Chem. Lett. (1997) 415.
[81] Z.Y. Xue, G.L. Schrader, J. Phys. Chem. B 103 (1999) 9459.
[82] A. Martin, V.N. Kalevaru, B. Lücke, Catal. Today 78 (2003) 311.
[83] G. Deo, I.E. Wachs, J. Catal. 146 (1994) 335.
[84] A. Pantazidis, A. Burrows, C.J. Kiely, C. Mirodatos, J. Catal. 177 (1998) 325.
[85] H.W. Zanthoff, W. Grünert, S. Buchholz, M. Heber, L. Stievano, F.E. Wagner, G.U. Wolf, J. Mol. Catal. A 162 (2000) 435.
[86] L.E. Briand, O.P. Tkachenko, M. Guraya, I.E. Wachs, W. Grünert, Surf. Int. Anal. 36 (2004) 238.
[87] L.E. Briand, O.P. Tkachenko, M. Guraya, X.T. Gao, I.E. Wachs, W. Grünert, J. Phys. Chem. B 108 (2004) 4823.
[88] (a) L.J. Burcham, L.E. Briand, I.E. Wachs, Langmuir 17 (2001) 6164;
(b) L.E. Briand, A. Hirt, I.E. Wachs, J. Catal. 202 (2001) 268.
[89] L.E. Briand, J.M. Jehng, L. Cornaglia, A.M. Hirt, I.E. Wachs, Catal. Today 78 (2003) 257.
[90] W. Grünert, L. Briand, O.P. Tkachenko, N.N. Tolkatchev, I.E. Wachs, Catalysis by metal oxides: comparison between bulk mixed oxides, supported oxides, oxide clusters, organometallic oxides and oxide single crystals, in: Proceedings of the Symposium at the 228th ACS Meeting, Philadelphia, 22–26 August 2004.
[91] J.A. Wilson, C.G. Hill, J.A. Dumesic, J. Mol. Catal. A 61 (1990) 333.
[92] M.O. Guerrero-Perez, J.L.G. Fierro, M.A. Vicente, M.A. Bañares, J. Catal. 206 (2002) 339.
[93] A. Andersson, S.L.T. Andersson, G. Centi, R.K. Graselli, M. Sanati, F. Trifirò, Stud. Surf. Sci. Catal. 75 (1993) 691.
[94] T. Birchall, A.W. Sleight, Inorg. Chem. 15 (4) (1976) 868.
[95] F.J. Berry, M.E. Brett, Inorg. Chim. Acta 7 (1983) L205.
[96] J.F. Brazdil, M.A. Toft, J.P. Bartek, R.G. Teller, R.M. Cyngier, Chem. Mater. 10 (1998) 4100.
[97] H.W. Zanthoff, W. Grünert, S. Bucholz, M. Heber, L. Stievano, F.E. Wagner, G.U. Wolft, J. Mol. Catal. A 162 (2000) 443.
[98] X. Gao, M.A. Bañares, I.E. Wachs, J. Catal. 188 (1999) 325.
[99] M.A. Bañares, M.V. Martinez-Huerta, X. Gao, J.L.G. Fierro, I.E. Wachs, Catal. Today 61 (2000) 295.
[100] X. Gao, J.-M. Jehng, I.E. Wachs, J. Catal. 209 (2002) 43.
[101] B.M. Weckhuysen, I.E. Wachs, J. Phys. Chem. 100 (1996) 14437.
[102] T.V.M. Rao, G. Deo, J.-M. Jehng, I.E. Wachs, Langmuir 20 (2004) 7159.
[103] S.J. Tinnemans, M.H.F. Kox, T.A. Nijhuis, T. Visser, B.M. Weckhuysen, Phys. Chem. Chem. Phys. 7 (2005) 211.
[104] G.L. Bourdon, F. Adar, M. Moreau, S. Morel, J. Reffner, A.-S. Mamede, C. Dujardin, E. Payen, Phys. Chem. Chem. Phys. 5 (2003) 4441.