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Gas Sensors

In Situ and Operando Spectroscopy for Assessing Mechanisms of Gas Sensing

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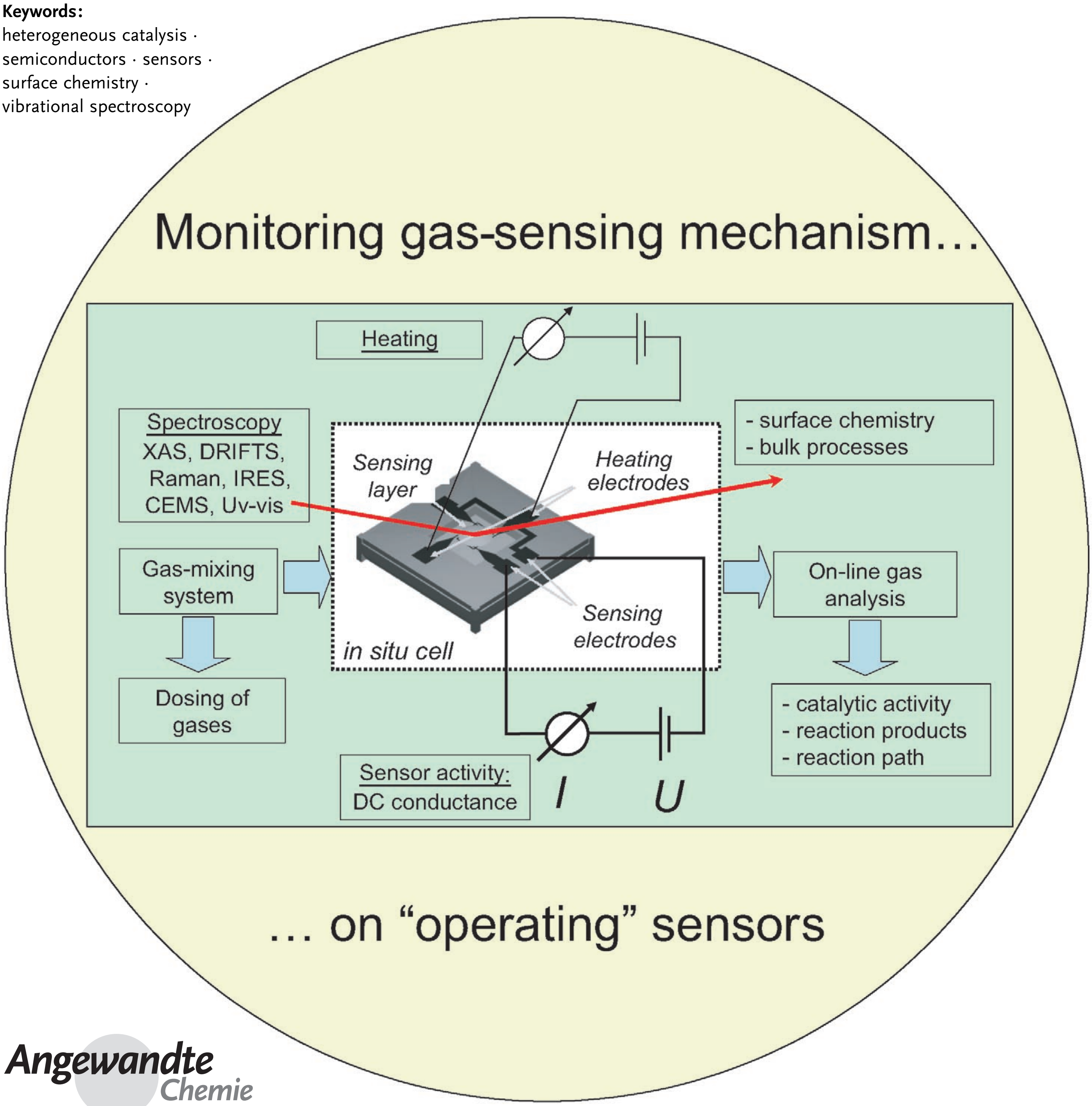

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The mechanistic description of gas sensing on inorganic, organic, and polymeric materials is of great scientific and technological interest. The understanding of surface and bulk reactions responsible for gas-sensing effects will lead to increased selectivity and sensitivity in the chemical determination of gases and thus to the development of better sensors. In recent years, spectroscopic tools have been developed to follow the physicochemical processes taking place in an active sensing element in real time and under operating conditions. Thus, the monitoring of the processes in "living" gas sensors is no longer an unsolvable problem. This Review gives an overview of in situ and operando spectroscopic techniques for the study of gas-sensing mechanisms on solid-state sensors.

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1. Introduction: In Situ and Operando Spectroscopy in Gas Sensing

Since the development of the first models of gas detection on metal-oxide-based gas sensors,[1,2] much effort has been made to describe the mechanism responsible for gas sensing (see, for example, references [3–5]). Despite progress in recent years, a number of key issues remain the subject of controversy, for example, the disagreement between electrical and spectroscopic investigations, as well as the lack of proven mechanistic description of the surface reactions involved in gas sensing. In this case, the "simultaneous measurement of the gas response and the determination of molecular adsorption properties are required for a better understanding of gas-sensing mechanisms".[6] This measurement can be done either on clean and well-defined surfaces in ultrahigh vacuum (UHV) conditions or at temperatures and pressures that mimic real sensor operating conditions ("in vitro"[7]). Continuous progress has been made during the past few years for the latter strategy, that is, the use of in situ and operando spectroscopic techniques.

The terms "in situ" and "operando" derive from the field of heterogeneous catalysis,[8–11] in which "in situ spectroscopy" represents spectroscopic techniques and measurements for studying catalysts in situ—"under reaction conditions … or conditions relevant to reaction conditions".[9] The term "operando spectroscopy" was introduced only recently to describe techniques that are able to characterize a "working" catalyst. This methodology combines in situ spectroscopic investigation with simultaneous monitoring of the catalytic performance (in the same experiment and on the same sample).[10,12–15] An "operando" experiment can be seen as a step towards a "perfect"[9] or "true"[11] in situ experiment that "would look inside an industrial reactor and reveal the most intimate details of a surface chemical reaction … and correlate the composition of the catalyst bed with simultaneous measurements of product distributions".[9] Such an experiment would be "conducted in such a way that the catalytic performance is measured simultaneously with the spectroscopic or structural property of the experiment".[11]

The difference as well as need for the differentiation between in situ and operando spectroscopy has been the subject of lively discussions during the past few years[10,12–17] and no consensus has yet been reached. For example, the term "in situ" has also been applied to characterization that "should be conducted of catalysts in their working state"[11] or on "a working catalyst".[10] Nevertheless, the term in situ spectroscopy is still much more widespread and much more common (see, for example, references [8,9,11]). The term "operando spectroscopy" or more generally "operando methodology" has, however, become increasingly popular in recent years (see, for example, references [10,12,13,16,18–20]). The simultaneous characterization of materials properties and the functionality of a device under operation has also become increasingly important in other fields of materials science (e.g., battery materials[21] and fuel cells[22,23]).

The present work attempts to review in situ and operando spectroscopic studies of gas sensing mechanisms on solid-state chemical sensors (for the brief introduction to sensors, see references [4,5,24–26]). In view of the points discussed above, we will herein differentiate the terms "in situ" and "operando" as shown in Figure 1 (Figure 2 demonstrates the

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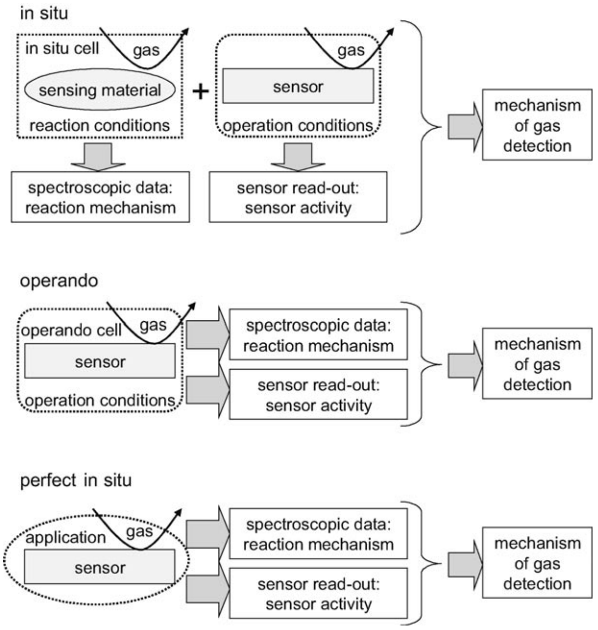

Figure 1. In situ and operando methodology in gas sensing.

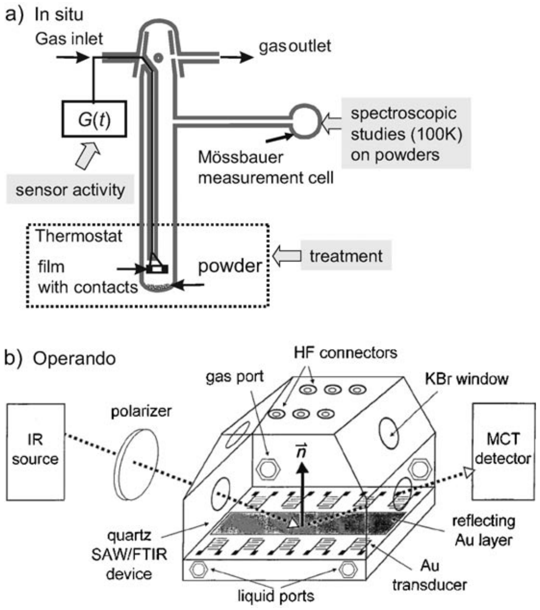

Figure 2. a) The in situ approach: The treatment of samples (sensors and powders) as well as electrical characterization of sensors is performed in the same conditions ("in situ"); the spectra, however, are recorded on powders after rapid quenching.[35] $G(t)$ = time-dependent conductivity. b) The operando approach: An in situ cell combines surface acoustic wave (SAW) sensor measurements with direct, in situ Fourier transform infrared external-reflectance spectroscopy (FT-IR-ERS) and probing surface of the sensing films during analyte exposure.[29,36]

difference between a typical in situ and operando experiment)[27]:

1) In situ spectroscopy: spectroscopic characterization of sensing material under operation conditions or conditions relevant to operation conditions; herein, the sensing performance of this material may be not characterized or may be characterized in a separate experiment;
2) Operando spectroscopy: spectroscopic characterization of an active sensing element in real time and under operating conditions with the simultaneous read-out of the sensor activity and simultaneous monitoring of gas composition.

These definitions determine the boundary conditions under which an "operando" experiment is performed:

1) on a *sensing element,* which itself is a complex device and consists of several parts: in solid-state devices with an electrical response, for example, the sensing layer is deposited onto a substrate to which electrodes for an electrical read-out are attached ("transducer"); therefore the assessment of their interfaces is of paramount importance for understanding the overall sensing mechanism;
2) *in real time:* a sensor is devised to respond to the changes in the gas atmosphere as fast as possible; accordingly, it demands a fast spectroscopic response;
3) *under operating conditions:* these can vary from ambient conditions (RT and atmospheric pressure) to high temperatures and pressures;
4) *with simultaneous read-out of sensor activity*: the gas concentration to be measured is transduced by the sensor into an electrical or other convenient output, depending on the modus operandi of the sensor (optical, mechanical, thermal, magnetic, electronic, or electrochemical) and the transducer technology;

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5) *with simultaneous monitoring of gas composition*; on-line gas analysis in gas sensing plays a twofold role: the output compositions and concentrations provide data about reaction products and possible reaction paths and the input concentration verifies the sensor input data (concentration of the component to be detected).

To the best of our knowledge, the first work on operando studies of the gas sensing mechanism, which appeared in 1995,[28] was the diffuse reflectance infrared Fourier transform spectroscopic (DRIFTS) characterization with simultaneous resistance measurements (i.e. "sensor performance"). CdGeON sensors operating at about 200 °C under atmospheric pressure were investigated upon exposure to different concentrations of oxygen in nitrogen. One of the most representative works, published in 1999, has the title "Reflectance Infrared Spectroscopy on Operating Surface Acoustic Wave Chemical Sensors during Exposure to Gas-Phase"[29] and demonstrates the application of operando methodology for polymer-based surface acoustic wave (SAW) sensors operated at room temperature (Figure 2b).

Already from these two examples one can see that different sensing materials as well as construction and operating conditions of sensors call for considerably different instrumentation, in situ cells, and spectroscopic methods. To cover all sensor types in one review would be very difficult, if not impossible. Accordingly, the present work is primarily devoted to the conductometric or resistive gas sensors based on semiconducting materials. These sensors are also called "gas-sensitive resistors",[30] "chemiresistors",[31] "metal-oxide-based gas sensors",[32] "oxidic semiconductor gas sensors",[33] or simply "semiconductor gas sensors".[3,34] All these definitions aim to emphasize the dependence of the semiconducting properties (mainly conductivity) of sensing materials (mainly oxides) upon the composition of gaseous environment. We will use the term "metal-oxide-based gas sensors" herein to underline the main focus on semiconducting metal oxides. This type of sensors has been chosen for this Review for the following reasons:

1) They are the most investigated group of sensors; the extensive number of experimental and theoretical works allow generalizations and conceptual developments to be recognized.
2) They are becoming increasingly relevant for mass-market applications; the understanding of surface and bulk reactions responsible for gas-sensing effects will lead to the increased selectivity and sensitivity in the chemical determination of gases and in the development of better sensors.
3) They are the most similar (besides calorimetric gas sensors or pellistors) to metal-oxide catalysts, as in both cases the elementary reaction steps involve chemisorption (e.g. of oxygen), and, in many cases, the sensing mechanism involves catalytic conversion (e.g. CO oxidation). For this reason, sensors and catalysts can be studied in similar ways, and the in situ and operando methodologies for heterogeneous catalysis and gas sensing can be directly compared.

This Review is organized as follows: Section 2 briefly describes the history, construction, and current understanding of the operating principle of metal-oxide-based gas sensors. Section 3 follows the different methodological approaches that have been dominant in the field over the past 50 years; the knowledge of this development helped us enormously to understand how the physicochemical processes taking place in a sensing element could be elucidated. Sections 4–6 cover the application of the in situ and operando spectroscopy to studies of the gas-sensing mechanism; the basic technical requirements as well as the typical construction of in situ cells and measurement procedures are also given. The discussion in these sections is not limited to the particular field of metal-oxide-based sensors, but addresses also some fundamental topics of gas-sensing studies. Finally, we compare spectroscopic studies of gas sensing and catalytic mechanisms on metal oxides (Section 7) and outline the potential for the future developments (Section 8).

2. Gas Sensors Based on Semiconducting Metal Oxides

Metal-oxide-based gas sensors reversibly change their conductivity in response to changes in gas concentration and thus provide information about the composition of the ambient atmosphere (Figure 3). They usually operate between 100 and 500 °C and have been mainly used in real-world conditions (at atmospheric pressure and at a high background oxygen concentration of 20.5 vol %). The sensor activity is expressed in terms of either sensor response (changes in resistance R) or sensor signal S (relative resistance changes, $S = R_{gas}/R_{air}$ or $S = R_{air}/R_{gas}$ for oxidizing and reducing gases, respectively; R_{gas} and R_{air} denote the sensor resistance in the presence and in the absence, respectively, of the target gas).

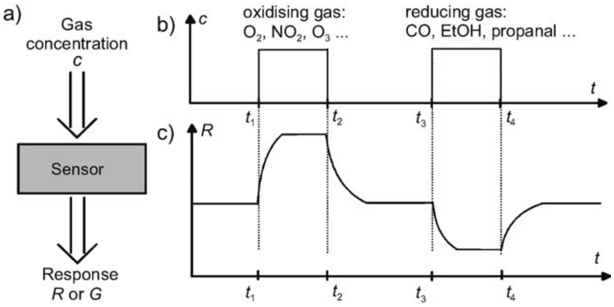

Figure 3. a) Metal-oxide-based gas sensor: The changes in the gas concentration (b; the gas is applied at t_1, t_3 and removed at t_2, t_4) lead to changes in the conductance G or resistance R of the sensor (c; modified from reference [37]).

2.1. Historical Remarks

Since the early 1920s, numerous investigations have demonstrated the influence of the gas atmosphere on conductivity, free carrier mobility, surface potential, and work function of a number of semiconductors (references [38–50] give a summary of early works). These studies led to the understanding that the surface of semiconductors is highly sensitive to chemical reactions and chemisorptive processes[40,51–57] and resulted eventually in the "theory of surface traps" (Brattain and Bardeen[58]), the "boundary layer theory of chemisorption" (Engell and Hauffe,[47,59,60] as well as Schottky[61]), and the "electron theory of chemisorption and catalysis on semiconductors" (Wolkenstein[42–44,62]). Thus the theoretical foundations for the subsequent development of metal-oxide-based gas sensors were laid.

Although it "was, in principle, a small step"[34] from this understanding to the use of semiconductors as gas sensors, the idea of using the changes in conductivity of a semiconducting metal oxide for gas detection was not conceived until the middle of the 1950s. The earliest written evidence[63] stems from a diploma thesis written in Erlangen in 1956 under the supervision of Mollwo and Heiland[64] and entitled "Oxygen detection in gases by changes in the conductivity of a semiconductor (ZnO)";[65] the results were discussed later in references [38,66]). In 1957, Heiland showed that the conducting surface layer on zinc-oxide crystals provides a very sensitive test for atomic hydrogen,[67] and Myasnikov demonstrated that a ZnO film can be used for highly sensitive oxygen analysis.[68,69] However, the conditions under which ZnO was able to operate as a sensing device were far from the real ambient conditions (and, accordingly, far from a practical application): the sensing effects were observed only upon exposure to oxygen or hydrogen under vacuum conditions, or after activation of the surface by heating in H_2 and under UHV conditions.[70]

The practical use of metal-oxide-based gas sensors in normal ambient conditions was not considered until 1962, when Seiyama et al. reported that ZnO film can be used as a detector of inflammable gases in air[71] (see also reference [72]), and Taguchi claimed that a sintered SnO_2 block can also work in the same way[73] (for the history of Taguchi gas sensors (TGS), see reference [74]). The latter approach became very successful and led to the formation of the first commercial sensor producer (Figaro Engineering Inc.), which began mass production and sale of the TGS in 1968 (Figure 4a).

Since then, many different metal oxides have been investigated as sensing materials (see reference [75] for a comprehensive review), but tin dioxide (SnO_2), either alone or "activated" with small quantities of noble metals (Pd, Pt, Au), has remained the most commonly used and the best-understood prototype material in commercial gas sensors[76] as well as in basic studies of the gas-sensing mechanism.[31,32,37,75–80]

2.2. Typical Construction

The most-advanced and best-performing metal-oxide-based gas sensors have a porous sensing layer based on annealed, nanoscaled oxide powders usually obtained through chemical routes (sol–gel, precipitation, chemical vapor deposition (CVD), FSP (FSP: flame spray pyrolysis))[31,75,81,82] and functionalized by adding small quantities of noble metals (Pd, Pt, or Au) in the form of surface additives. In a typical metal-oxide-based gas sensor, the porous sensing layer is deposited on the transducer surface (e.g. Si_3N_4, Al_2O_3, Si/SiO_x) carrying the electrodes and an integrated heater (Figure 4b). The latter helps to achieve the typical sensor operation temperature on the order of 100 to 500 °C. Metal electrodes (usually Pt or Au) are fabricated to enable conductance (or resistance) measurement of the sensing material (Figure 4c).

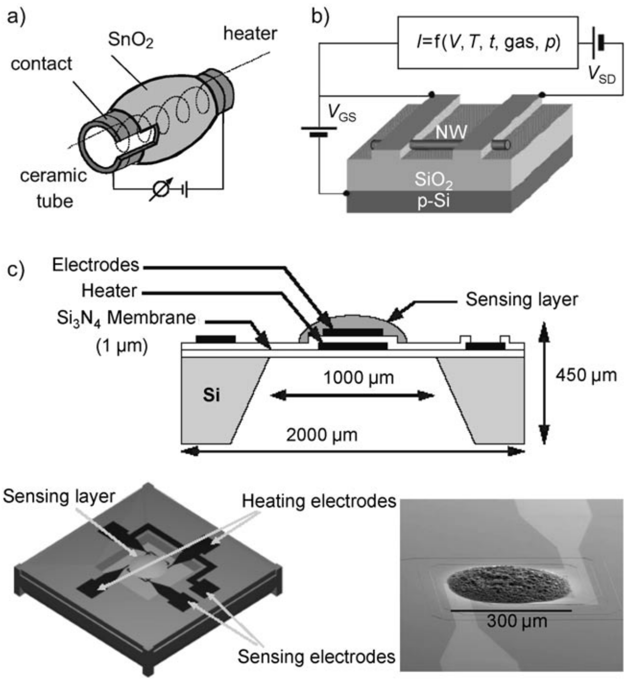

Figure 4. Typical metal-oxide sensing elements: a) The Figaro-Taguchi-type (TGS) sensor; b) a SnO_2 nanowire (NW) gas sensor configured as a field-effect transistor (FET)[83] (thickness of SiO_2 layer: 300 nm; p-Si = p-doped silicon, V_{GS} = gate-to-source voltage, V_{SD} = source-to-drain voltage); c) micromachined sensing element; top: side view, left bottom: 3D view, right bottom: microscopy image of the sensor.[84]

A significant amount of research is currently directed toward sensor miniaturization and microfabrication of metal-oxide sensors. One of the current trends is the full integration of microfabricated or MEMS-type (MEMS: micro-electro-mechanical systems) sensors with the associated driving and signal conditioning electronics on a single chip, preferably in CMOS technology (CMOS: complementary metal-oxide semiconductor).[85,81] Sensor microfabrication requires small film thicknesses (around 1 μm) and the small lateral spot sizes (of 100 μm) to use the smallest possible quantity of the sensing material. The second line of development is directed towards a nanosensor constructed from either a few nanoparticles or an individual nanowire (or nanobelt—a quasi-one-dimensional (Q1D) nanostructure; see reference [86] and references therein). In this case, however, a field-effect transistor (FET) (see Figure 4b) is the preferred setup rather than a resistor.

2.3. Mechanism of Gas Detection

The operation of metal-oxide-based gas sensors is currently described by two different models. The first considers only the space–charge effects/changes of the electric surface potential that result from the "ionosorption" of gaseous molecules (ionosorption model). The second model explains the sensing effects by changes in the oxygen stoichiometry, that is, by the variation of the amount of the (sub-)surface oxygen vacancies and their ionization (reduction–reoxidation mechanism, Table 1). The origin of both models can be traced back to the 1950s, that is, to the mechanistic description of reactions in and on solid materials;[48,49] since then they have been repeatedly discussed in mechanistic studies (see, for example, references [2,66,87,88]). It must also be kept in mind that the mechanism may be influenced significantly by the materials and operating conditions (e.g. temperature, composition of gaseous phase, hydroxylation of the surface).

2.3.1. Ionosorption Model

Key in the mechanistic description of gas sensing is "oxygen ionosorption" and the reaction of reducing gases with ionosorbed oxygen ions. On an n-type semiconductor (e.g. SnO_2), oxygen ions are formed through the transfer of electrons from the conduction band (CB) and are electrostatically stabilized in the vicinity of the surface (for details, see our recent review article[89]). The application of these considerations is limited to the temperature range in which diffusion processes do not take place. Accordingly, the operation of SnO_2-based sensors is described as follows: atmospheric oxygen adsorbs on SnO_2 as molecular ($O_2{}^{-}{}_{ads}$) and atomic ($O^{-}{}_{ads}$, $O^{2-}{}_{ads}$) ions, which trap electrons from the conduction band; reducing gases such as CO react with the oxygen ions (according to either a Eley–Rideal or Langmuir–Hinshelwood mechanism) and release electrons, which return to the conduction band. In an oxygen-free atmosphere, CO acts as electron donor: it is adsorbed as a CO^{+} ion, thus inserting an electron into the conduction band. All these processes involve electrons in the conduction band and thus influence the electrical conductivity. However, contradictions arises when these considerations are compared with spectroscopic observations. A critical look at the available experimental data shows that this model is based mainly on phenomenological measurements. Although it has been sought for a long time, there is not yet any convincing spectroscopic evidence for "ionosorption". Neither the superoxide ion $O_2{}^{-}$, the charged atomic oxygen ion O^{-}, peroxide ions $O_2{}^{2-}$, nor CO^{+} have been observed under real working conditions of sensors.[89]

2.3.2. Oxygen-Vacancy Model (Reduction–Reoxidation Mechanism)

This model focuses on oxygen vacancies at the surface, which are considered to be "the determining factor in the chemiresistive behavior".[90] Tin dioxide, the most extensively investigated sensing material, is oxygen-deficient and, therefore, an n-type semiconductor, whose oxygen vacancies act as electron donors. Alternate reduction and reoxidation of the surface by gaseous oxygen (Mars–van Krevelen mechanism) control the surface conductivity and therefore the overall sensing behavior. In this model, the mechanism of CO detection is represented as follows: 1) CO removes oxygen from the surface of the lattice to give CO_2, thereby producing an oxygen vacancy; 2) the vacancy becomes ionized, thereby introducing electrons into the conduction band and increasing the conductivity; 3) if oxygen is present, it fills the vacancy; in this process one or more electrons are taken from the conduction band, which results in the decrease in conductivity.

Numerous experimental and theoretical works have evaluated this explanation of gas-sensing effects (see, for example, references [86,90–95]), and it dominates in almost all spectroscopic studies (see, for example, references [35,96–100]). Several problems, however, are often not considered or avoided by the nonrealistic experimental conditions. Let us consider an example of CO detection in the oxygen-free conditions (alternating CO/N_2 and N_2 flows): What happens when CO is removed from the surrounding atmosphere? From electrical measurements one knows that the sensor resistance (or conductance) recovers its initial value. How-

Table 1: Gas-sensing mechanism on SnO_2 according to the ionosorption and oxygen-vacancy models.[a]

Gas/mixture	Ionosorption model	Oxygen-vacancy model
oxygen	$O_{2(ads)} + e^{-}(CB) \rightleftarrows O_2{}^{-}{}_{(ads)}$ $O_2{}^{-}{}_{(ads)} + e^{-}(CB) \rightleftarrows O_2{}^{2-}{}_{(ads)} \rightleftarrows 2\,O^{-}{}_{(ads)}$	$2\,V_O{}^{\bullet} + O_{2(gas)} + 2\,e^{-}(CB) \rightleftarrows 2\,O_O{}^{x}$
CO/presence of oxygen	$CO_{(gas)} + O^{-}{}_{(ads)} \rightleftarrows CO_{2(gas)} + e^{-}(CB)$	$CO_{(gas)} + O_O{}^{\times} \rightleftarrows CO_{2(gas)} + V_O{}^{x}$ $V_O{}^{x} \rightleftarrows V_O{}^{\bullet} + e^{-}(CB)$
CO/absence of oxygen	$CO_{(gas)} \rightleftarrows CO^{+}{}_{(ads)} + e^{-}(CB)$	$V_O{}^{\bullet} \rightleftarrows V_O{}^{\bullet\bullet} + e^{-}(CB)$
NO_2	$NO_{2(gas)} + e^{-}(CB) \rightleftarrows NO_2{}^{-}{}_{(ads)}$	$NO_{2(gas)} + V_O{}^{\bullet} \rightleftarrows NO_2{}^{-}{}_{(ads)} + V_O{}^{\bullet\bullet}$ $2\,NO_{(gas)} + O_2{}^{-}{}_{(ads)} + V_O{}^{\bullet} \rightleftarrows 2\,NO_3{}^{-}{}_{(ads)} + V_O{}^{\bullet\bullet}$
water vapor	$H_2O_{(gas)} + O^{-}{}_{(ads)} + 2\,Sn_{Sn}{}^{x} \rightleftarrows 2(Sn_{Sn}{}^{x}\text{–}OH) + e^{-}(CB)$ $H_2O_{(gas)} + Sn_{Sn}{}^{x} + O_O{}^{\times} \rightleftarrows (Sn_{Sn}{}^{x}\text{–}OH) + OH_O{}^{\bullet} + e^{-}(CB)$	$H_2O_{(gas)} + 2\,Sn_{Sn}{}^{x} + O_O{}^{x} \rightleftarrows 2(Sn_{Sn}{}^{x}\text{–}OH) + V_O{}^{\bullet} + e^{-}(CB)$

[a] CB: conduction band, V_O: oxygen vacancy. The Kröger–Vink notation is used to show the charges of the lattice atoms/species (Sn, O, OH); for adsorbed species and electrons the "real" charges are shown; $V_O{}^{\times}$: neutral (i.e., two electrons localized in an oxygen vacancy), $V_O{}^{\bullet}$: singly ionized oxygen vacancy, $V_O{}^{\bullet\bullet}$: doubly ionized oxygen vacancy, $Sn_{Sn}{}^{\times}$: tin ion (Sn^{4+}) on a tin lattice site, $OH_O{}^{\bullet}$: hydroxide ion (OH^{-}) on an oxygen lattice site.

ever, within the framework of the reduction–reoxidation mechanism, gaseous oxygen is required for the reverse process (“vacancy refilling”). Unfortunately, the consideration of this problem has been avoided in spectroscopic studies by alternating CO/N_2 (or Ar) and O_2/N_2 (or Ar) flows, whereas “realistic” conditions require alternating CO/N_2 (or Ar) and N_2 (or Ar) flows.

The second problem concerns the kinetics of oxygen exchange at the surface, which is considerably slow.[101] The third problem is related to the ionization of oxygen vacancies and consequently to the diffusion processes in the oxide lattice. For SnO_2, for example, it is assumed that the surface defects do not act as electron donors; they have to migrate a small distance into the bulk to become ionized.[91] The diffusion coefficients for this process are low, and, accordingly, the defects are immobilized at the operating temperatures.[92–95,102,103] Nevertheless, diffusion at grain boundaries and at the surface can be much faster than bulk diffusion.[49]

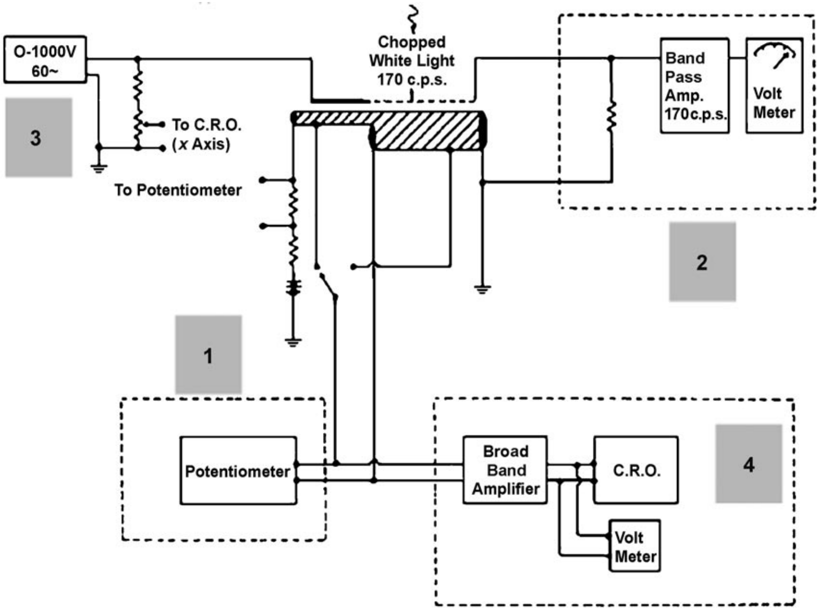

Figure 5. Apparatus for the study of surface conductance (1), work function (CPD) changes (2), field effect (3), and photoconductivity (4) of “surface lifetime, with changes in ambient” (1954).[108] 60~: ac (60 Hz), C.R.O.: cathode ray oscilloscope.

3. From “Prototype Structures” to “Operating Sensors”

The “crossing of interests”[104] and “bridges of physics and of chemistry across the semiconductor surface”[105] determined experimental methodology applied for the gas–semiconductor studies in general and gas sensing studies in particular in the course of the last 50 years. “The physicist’s attention was drawn to it mainly due to the influence of the boundary on the behaviour of the atmosphere of electrical carriers, electrons and holes within the solid; […] the chemist has been concerned with its influence on the atmosphere of atoms and molecules externally surrounding the solid.”[105,106]

Initially, the influence of adsorbed gas molecules on electrical properties has been investigated by means of conductivity, Hall effect, contact potential difference (CPD), and field effect measurements. These investigations were interpreted in terms of semiconductor theory. ZnO (and Ge in early works) served as a model compound in these studies.[107] Considerable progress was achieved in both theoretical modeling (e.g. the first model for gas detection on semiconducting metal oxides[1]) as well as the development of new methods. The idea of combining two or more (in this case, electrical) techniques and applying them simultaneously in situ was pioneered by this approach. As early as 1954, measurements of surface conductance, field effect, photoconductivity, and the CPD (work-function changes) were combined to characterize the interaction of oxygen with a Ge surface under changing gaseous environments (Figure 5).[108] Several years later, a combination of CPD and conductivity measurements was used to determine the dipole moment of the adsorbate molecule; in this way, the neutral and charged forms of an adsorbed gas could be differentiated[109,110] (see also the summary in references [50,111,112]).

Later it became evident that:

1) Polycrystalline materials are considerably more active than single crystals;[38]
2) The activity of polycrystalline materials depends strongly on their preparation and pretreatment;[38]
3) It is not possible to interpret the results on polycrystalline samples in the light of single crystal measurements.[57]

Accordingly, it was understood that the catalyzed reactions and the surface conductivity of the semiconductor catalysts should be followed simultaneously. The only difficulty was that polycrystalline specimens are useful for adsorption and catalysis because of their large surface, but single crystals are needed for precise measurements of surface conductivity.[113]

This understanding resulted in two different methodologies; the first one—“surface science methodology”—involved spectroscopic and electrical characterization of chemisorption and catalytic reactions on well-defined surfaces[113,114] (single crystals and clean surfaces). The second on focused the combination of electrical measurements with spectroscopic investigations applied to polycrystalline, high-surface-area materials.

More specifically, the “surface science” methodology has aimed at the “detailed atomistic understanding of charge transfer reactions between semiconductor surfaces and adsorbing particles”[115] through surface analysis techniques—thermal desorption, mass spectrometry, and measurements of conductivity and work function (Figure 6)[114]—applied to the same crystal under vacuum (usually

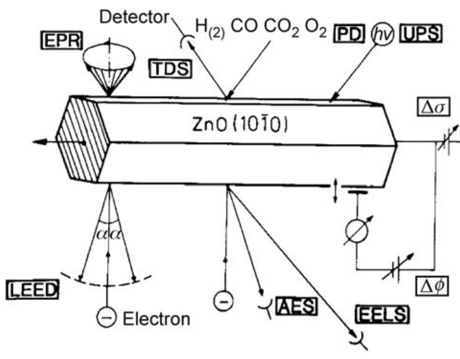

Figure 6. Experimental techniques for research on prototypical semiconductor surfaces: EPR: electron paramagnetic resonance, TDS: thermal desorption spectroscopy, PD: photodesorption, UPS: ultraviolet photoemission spectroscopy, EELS: electron-energy-loss spectroscopy, LEED: low-energy-electron spectroscopy, AES = Auger electron spectroscopy; surface conductivity and work function measurements.[120] ($\Delta\sigma$ = surface conductivity measurements, $\Delta\phi$ = work-function potential (Kelvin probe))

UHV).[91,116] Most of these investigations involved ZnO (see, for example, reference [116] and the summary in references [115,117]), TiO_2 (see, for example, reference [118] and the summary in references [115,117]), and SnO_2 (see, for example, references [88,91,119]), and it was mainly through work on these materials that the understanding of gas–oxide interactions was advanced at that time.

The first systematic methodological approach (“design concept for chemical sensors”) in gas-sensing studies was explicitly formulated in 1985 in a series of papers entitled “Development of chemical sensors: empirical art or systematic research?”[121] (see also references [115,122,123]). The underlying concept was that by “studying the surface of single crystals under well-defined conditions, one might try to achieve a better separation of parameters influencing the properties of gas sensors”.[91] The reactions were addressed by surface spectroscopic methods under UHV conditions on well-defined “prototype” structures while the sensor performance was tested under realistic measuring conditions on structures of practical importance (“sensors”).

This “comparative approach” advanced the basic understanding of surface reactions and conduction mechanisms responsible for gas sensing. However, it also showed the limits of surface science in gas-sensing studies and led to the understanding that if spectroscopic and electrical data are not obtained simultaneously, they must be obtained under the same conditions and on identical samples (Figure 7). A comprehensive description of surface reactions on SnO_2 published in 1989 resulted from simultaneous thermal-desorption spectroscopy (TDS; i.e. reactive scattering of a molecular beam) and conductance measurements.[91] These measurements were applied to SnO_2 single crystals and thin evaporated films exposed to a certain dose of AcOH, CO, or CH_4 in UHV conditions at working temperature of sensors.

The comeback of surface-science methods—as “a novel experimental approach for studying the gas response mechanism”[6]—has been observed recently.[6,124–127] Also the recent investigations performed under vacuum conditions on individual Q1D nanostructures (i.e. single crystals!) (see, for example, references [128–130] and review article in reference [86]) as well as the simultaneous conductance and temperature-programmed desorption (TPD)[131] investigations can be attributed to surface-science methodology.

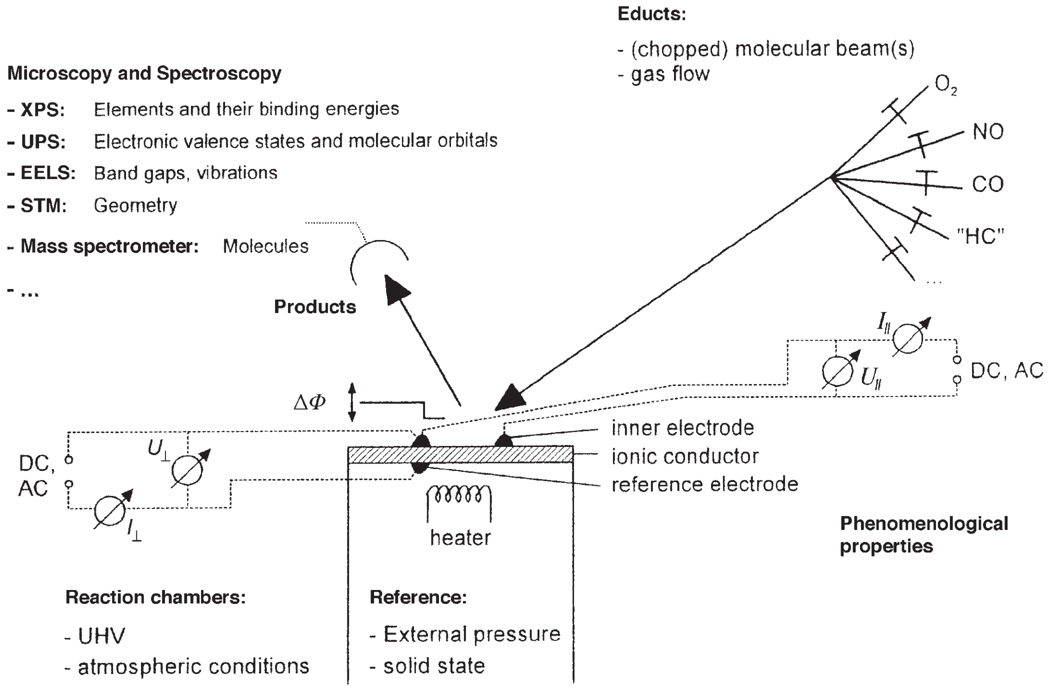

Figure 7. Experimental setup for monitoring charge-transfer reactions at interfaces on gas exposure under UHV conditions or ordinary pressure conditions (with the exception of spectroscopic tools) by monitoring phenomenological properties such as dc and ac conductance, work function $\Delta\Phi$, etc.; product formation by means of mass-spectrometry; or microscopic and spectroscopic properties.[123]

These investigations will undoubtedly lead to extremely detailed results, but extrapolation of the data from ideal to real conditions is not always straightforward and in many cases can even be misleading.

Development within the second line of activities (second methodology) has focused on the combination of electrical measurements with spectroscopic investigations of catalysis on polycrystalline, high-surface-area materials with the aim to "link semiconductor studies with catalytic studies".[46] However, most of the studies were performed under conditions far from the real working conditions of sensors (for a summary of numerous studies on semiconducting metal oxides, see references [41,50,112]). Besides spectroscopic and catalytic (kinetic) investigations (SnO_2: kinetic studies of CO oxidation,[132] IR spectroscopic studies of water, CO_2, and CO adsorption,[133] (summarized in reference [134]), EPR investigations of oxygen adsorption,[135] (reviewed in references [136,137])), the improvements were concentrated on devising systems and in situ cells for combined (i.e., performed under the same conditions on "identical" samples) and simultaneous electrical, catalytic, and spectral investigations (Table 2).

These activities, however, were overlooked by the sensor community at that time, as in situ electrical characterization of realistic ("polycrystalline") samples, namely, Hall effect measurements (1982[144]), changes in work function (CPD) by the Kelvin method (1983[145]), ac impedance spectroscopy (1991[146,147]), simultaneous work function change and conductance measurements (1991[148]) were preferred for studying the mechanisms of operating sensors. Later, this approach was followed systematically in the number of works (reviewed in references [32,149], recent works in references [150–154] and references therein) to elucidate a mechanism of gas detection on SnO_2-based sensors. Local electronic properties (e.g., the density of states in the region near the band gap) of a sensing material were determined by scanning tunneling microscopy and spectroscopy (STM-STS) in vacuum conditions[155–157] or under N_2, CO, and NO_2 at room temperature.[158]

By the end of the 1990s, the spectroscopic techniques for gas-sensing studies were differentiated according to conditions under which they can be applied: those that may be applied "under in situ real operating conditions of the sensors"[159] and those that may be applied "under ideal conditions far away from real practical world".[159] This differentiation subsequently resulted in the systematic combination of phenomenological and spectroscopic measurement techniques under working conditions of sensors,[32] and thus in the in situ and operando methodology.

Table 2: Early works on combining in situ spectroscopic and phenomenological techniques.

Year	Technique
1970	in situ cell for simultaneous measurement of infrared spectra and electrical conductivity (of Ni film) at room temperature upon exposure to CO and N_2[138]
1975	application of a spectroscopic method (EPR) and an electrical technique (Hall effect measurements) on identical polycrystalline samples (SnO_2) treated in the same way (under in situ conditions) to study oxygen adsorption[135]
1976	in situ cell for simultaneous study of infrared spectra and electrical conductivity of adsorbents (H_2O) on heated samples (SiO_2)[139]
1978	investigation of the mechanism of CO detection by combined catalytic conversion and conductance measurements at atmospheric pressure on polycrystalline samples (Co_3O_4) synthesized and prepared in the same way[140]
1979	TPD, EPR, and conductivity measurements for investigation of the mechanism of gas detection (influence of O_2, H_2O, H_2) on polycrystalline samples (SnO_2) synthesized and prepared in the same way and treated under in situ conditions[141]
1981	investigation of the mechanism of conductance changes in metal oxides for the detection and measuring of atmospheric pollutants (CO detection on polycrystalline ZnO) by simultaneous infrared and conductance measurements[142]
1985	in situ high-temperature conversion CEMS[a] measurement on α- and γ-Fe_2O_3 pellets ("sensors") upon gas exposure to elucidate the mechanism of the gas-sensing properties[143]

[a] CEMS = conversion electron Mössbauer spectroscopy.

4. In Situ and Operando Methodology: Basic Requirements and Limitations

The operando methodology couples electrical ("phenomenological") and spectroscopic techniques and aims to correlate the sensor activity with the spectroscopic data obtained under the same conditions on the same sample (Figure 8). In an ideal case, one would obtain four types of information: 1) gas-phase changes (and reaction products) from on-line gas analysis, 2) species adsorbed on the surface, 3) changes in the oxide surface and lattice, and 4) sensor activity. However, in practice, all these pieces of information are seldom obtained.

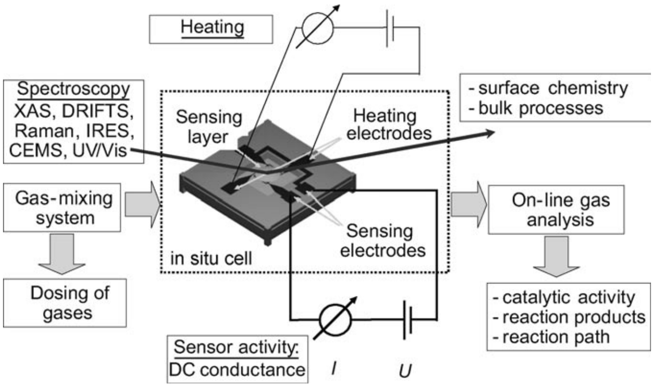

Figure 8. Methodological approach for simultaneous spectroscopic and electrical ("phenomenological") characterization of gas sensors based on semiconducting metal oxides.

The different applications, operational principle, and construction of sensing devices requires spectroscopic methods for their study different from those for the study of catalysts:

1) Sensors are designed for detecting toxic gases in low concentrations (e.g. below 50 ppm for CO, below 1 ppm for NO_2 and below 0.1 ppm for O_3); this requires sensitive spectroscopic methods.
2) A sensor is a complex device. Spectroscopic studies (in an ideal case) have to be done on the complete device, but several physicochemical effects complicate the interpretation of the spectroscopic and electrical measurements. For example, in the case of the porous metal-oxide layer, the gas penetrates into the sensitive layer down to the substrate and electrodes. The interaction with the gas can therefore take place at the following places: a) at the surface of individual particles, b) at the intergrain boundaries, c) at the interface between particles and the substrate, d) at the interface between particles and the electrodes, e) at the three-phase boundary interface between particles, electrodes, and substrate, f) at the heater, and g) at the substrate (Figure 9). The situation will become even more complicated when the metal oxide is activated with small particles (clusters) of noble metals. Unfortunately, the influence of these effects is usually underestimated or omitted in spectroscopic studies.
3) The amount of sensing material in a sensor is limited. For example, the porous sensing layer in microsensors is about 300 μm in diameter and about 1 μm thick and thus requires high-performance spectroscopic methods and in situ cells for investigations. The development of in situ and operando methods for sensors based on individual nanowires seems to be a very challenging task.

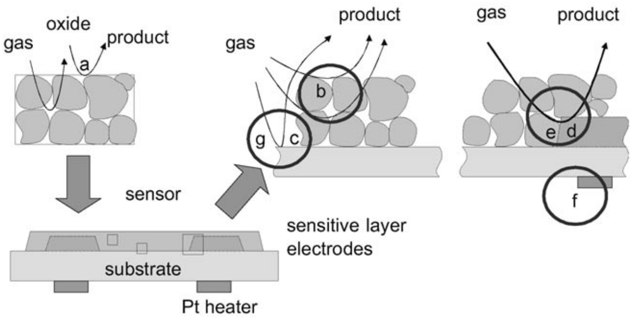

Figure 9. Possible ways in which a gas can interact with a porous metal-oxide sensing layer (see text for details; modified from reference [32]).

Table 3: Spectroscopic gas-sensing studies.

Electrical measurements	Spectroscopy	Conditions	Approach
sensors		simultaneously	operando
pellets/self-supporting disks		simultaneously	operando-pellets
sensors		in parallel on nominally identical samples; identical conditions	parallel-sensors
sensors	powders, films, pellets, or self-supporting disks	in parallel on different samples; identical conditions	parallel
		in parallel on different samples, treatment in identical conditions, spectroscopic measurements at low temperatures (quenching)	parallel-quenching

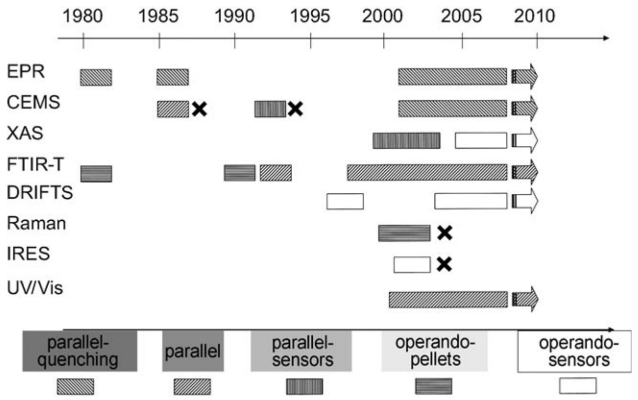

Figure 10. Development of in situ and operando techniques for gas-sensing studies on semiconducting metal oxides. ×: no further works.

Because of these technical and instrumental problems, several simplifications have been implemented in the spectroscopic study of gas-sensing mechanisms (Table 3, Figure 10). In the "pellet" approach, the simultaneous spectroscopic and electrical measurements are made on a pressed pellet (or self-supporting disk) of a sensing material. In the parallel approach, the spectroscopic and electrical measurements are performed under identical conditions (not simultaneously) on the identical samples (the "sensors"); in a more simplified version, the samples are treated under identical conditions, but the electrical measurements are made on sensors/films and the spectroscopic measurements are made on powders/pellets. In the "quenching" approach, the treatment of samples as well as electrical characterization of films or sensors is performed in situ, the spectra are recorded at low temperatures (e.g., −196 °C or room temperature) on powders after rapid quenching.

Accordingly, a variety of cells for in situ and operando spectroscopy have been developed over the years, all of which, however, must meet basis requirements: Firstly, it must be able to read-out the sensor as well as heat the sample; the electrical connections for the sensing electrodes and the heating element should not interfere with the simultaneous spectroscopic characterization. Secondly, the cell must allow high-temperature in situ treatments and spectroscopy at high temperatures in controllable gas atmospheres. Some typical designs of cells for in situ and operando investigations were already shown in Figure 2; some of these will be discussed in the next section.

5. Application of In Situ and Operando Spectroscopy to Gas-Sensing Studies

The application of different spectroscopic methods is directly related to the state-of-the-art understanding of gas-sensing mechanism (Table 4).

Table 4: Spectroscopic techniques for gas-sensing studies.

Species/processes	Methods[a]
charged oxygen species	EPR, vibrational spectroscopy
adsorbed molecular water and hydroxy groups	vibrational spectroscopy
adsorbed surface species (carbonates, carboxylates, etc.)	vibrational spectroscopy, NMR spectroscopy
oxygen vacancies (singly ionized, paramagnetic)	EPR spectroscopy
oxygen vacancies (singly and doubly ionized)	DR-UV/Vis/NIR spectroscopy
metal cations in lower oxidation state (Sn^{2+}, Sn^{3+}, Mo^{5+}, etc.)	CEMS, XAS, DR-UV/Vis/NIR, EPR spectroscopy
reaction products	gas sensors, MS, PAS, gas FTIR, specific gas analyzers, DRIFTS/IRES in pores of the sensing material

[a] IRES = IR emission spectroscopy, DR = diffuse reflectance, PAS = photoacoustic spectroscopy, XAS = X-ray absorption spectroscopy.

5.1. Vibrational spectroscopy

Because of their relative simplicity and wide applicability for monitoring surface reactions on metal oxides,[160] vibrational spectroscopic methods combined with simultaneous monitoring of conductance/resistance changes are most frequently used in gas-sensing research. These include infrared spectroscopy (transmission-absorption) on pellets and self-supporting disks of sensing material[142,161,162], Raman spectroscopy on pressed pellets[163–165], diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS),[28,166–170] and emission infrared spectroscopy (IRES)[99,171] on thick film sensors (Figure 11).

For the transmission-absorption measurements upon exposure to gas in a vacuum[142,162] or at atmospheric pressure,[161] a twin-beam cell was used to cancel out the infrared absorption of gas-phase species. As well as observing surface processes and identifying active sites, reaction intermediates, and spectator species, FTIR spectroscopy can also be used to monitor the absorption of free charge carriers in semiconducting metal oxides.[172]

DRIFTS and IRES provide a very important advantage over conventional FTIR spectroscopy in that they can be applied directly on the heated sensing element, and hence the spectroscopic and electrical data can be obtained simultaneously and directly (on the thick films of the sensing layer). DRIFTS also allows observation of the gaseous molecules in the pores of the sensor material,[168,170] which enables on-line (in situ) analysis of possible reaction products. The radiation emitted by the heated sensor is used as an IR source in IRES; the emitted radiation is collected from only a small area (ca. 0.25 mm^2) to ensure that the observed sample surface is

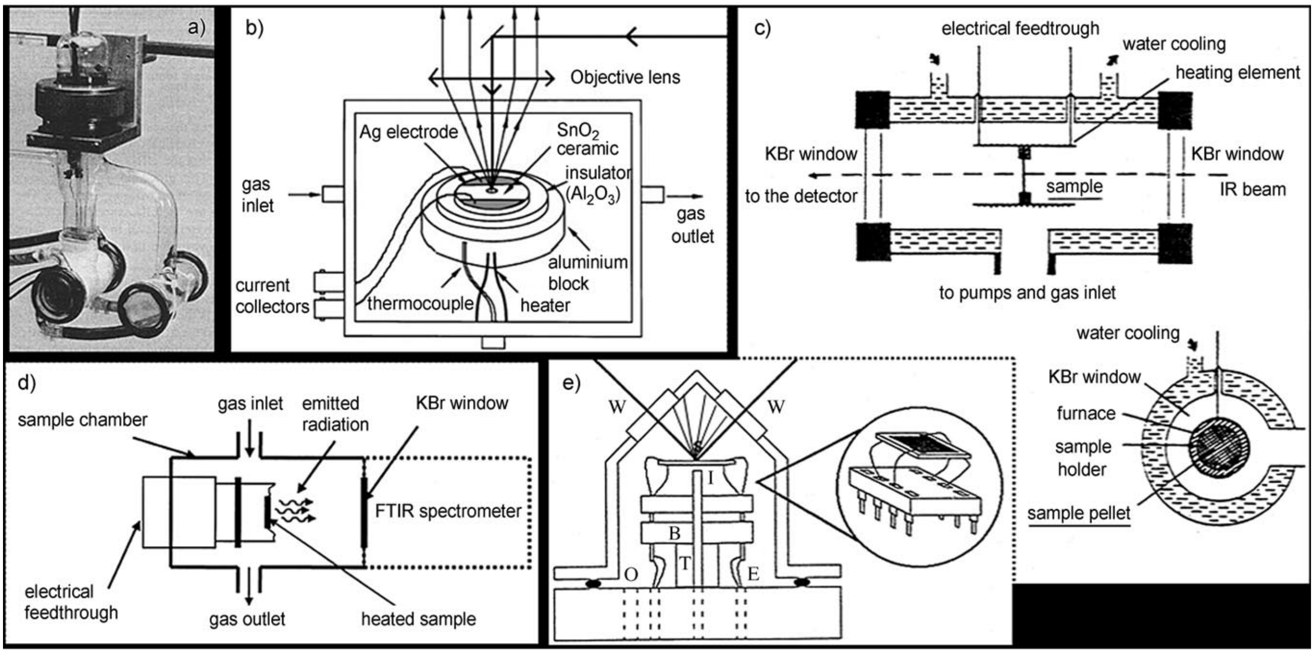

Figure 11. In situ and operando cells for simultaneous electrical and spectroscopic measurements: a) twin-beam cell for avoiding infrared absorptions of gas-phase species; transmission-absorption FTIR spectroscopy on self-supporting disks;[161] b) Raman spectroscopy on pellets;[163] c) transmission-absorption FTIR spectroscopy on pellets;[162] d) DRIFTS on sensors;[28] e) IRES on sensors.[171] I: gas inlet, O: gas outlet, B: sample holder plug, E: electrical feedthroughs, T: ceramic spacer, W: ZnSe windows, S: sample.

homogeneous in temperature. The same advantage is also provided by Raman spectroscopy (micro-Raman),[163–165] in which the characterization can be performed rapidly at various points of the sample to monitor the behavior of the interfaces (e.g. electrode/sensing material).

5.2. X-ray Absorption Spectroscopy (XAS)

X-ray absorption spectroscopy (XAS) (extended X-ray absorption fine structure (EXAFS) and X-ray absorption near-edge structure (XANES)) is one of the most powerful methods providing information about electronic (oxidation states of elements) and structural properties (coordination environment of the elements) of the sensing material (Figure 12 a) and is especially useful for monitoring changes associated with the chemical reactivity of functional surface additives, such as, noble metals (Pt, Pt, Au). It has been applied in fluorescence mode for in situ characterization of sensors (at atmospheric pressure and operating temperature under exposure to gas): The Pt L_3 white line[173,174] was monitored to perform the electrical measurements on the same sample either in a cooling run[173,174] or simultaneously.[175] The Sn L and Pd K edges were monitored simultaneously with conductance and catalytic conversion measurements.[176]

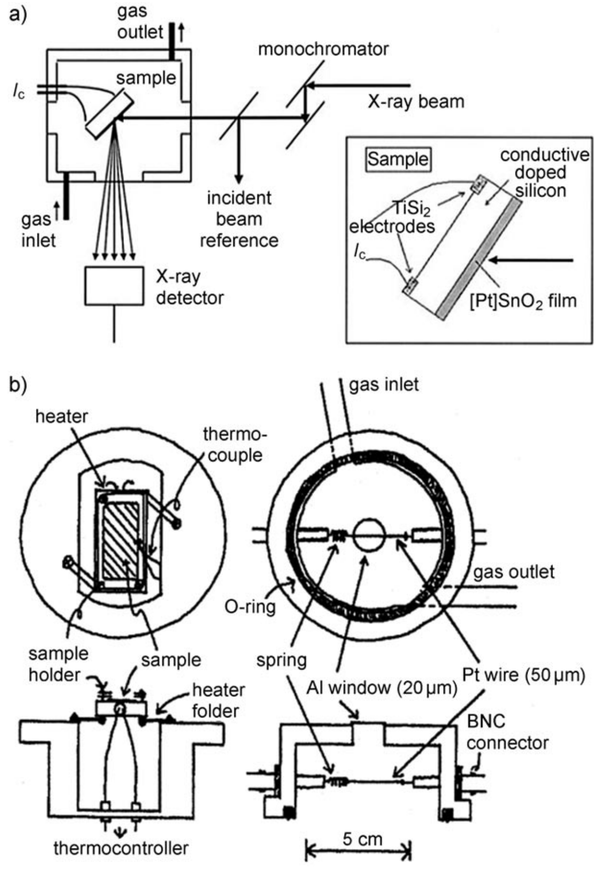

Figure 12. In situ cells for combined spectroscopic and electrical characterization of sensors: a) XAS,[173,174] (I_c: monitored current used to heat the conductive silicon substrate); b) CEMS.[143]

5.3. Mössbauer Spectroscopy

Mössbauer spectroscopy can be used to determine oxidation states and to follow the reaction kinetics of sensing materials. The great advantage of Mössbauer spectroscopy is high penetrating power of the γ photons, which makes the technique particularly suited for in situ studies.[177] Its application, however, is limited to a small number of elements that exhibit a Mössbauer effect: these include the isotopes ^{119}Sn, ^{57}Fe, and ^{182}W, so Mössbauer spectroscopic investigations can be performed on SnO_2, Fe_2O_3, and WO_3, important materials for gas sensing. In situ transmission Mössbauer spectroscopic investigations were performed on SnO_2 powders[35] to clarify the kinetics of the conductance change under exposure to reducing gases. The treatment of samples as well as electrical characterization of the films was performed in situ, and the Mössbauer spectra (^{119}Sn) were recorded at −173 °C on powders after rapid quenching (see Figure 1 a). The development of a gas-flow proportional counter enabled high-temperature in situ (backscatter) conversion electron Mössbauer spectroscopic (CEMS) studies of the sensors.[143,178,179] Detection of the conversion electrons yields significant information about the chemical composition of the surface (Figure 12 b).[7,180]

5.4. Electronic Spectroscopy

UV/Vis/NIR spectroscopy provides information about electron transitions. Relevant for gas sensing are those associated with the oxygen vacancies (e.g. ionization) as well as d–d and charge-transfer transitions in transition-metal oxides such as WO_3, MoO_3. Diffuse reflectance spectroscopy (DRS) was used in gas-sensing studies for the investigation of powders and thick films. The treatment of powders and thick films (MoO_3, WO_3, and mixed samples,[97,181,182] as well as Cr/Sn oxides[183]) was performed in situ (at operating temperature, under gas exposure), but the spectra were recorded at room temperature. Electrical data were obtained on thick films in a separate experiment.

5.5. EPR Spectroscopy

Electron paramagnetic resonance (EPR) spectroscopy is an especially useful technique for the investigation of gas sensing,[96] as it is able to detect charged molecular and atomic adsorbed oxygen ($O_2^{-}{}_{ads}$ and O^{-}) as well as paramagnetic oxygen vacancies ($V_O^{\bullet}$), which are suspected to be key species in the electronic response of metal oxides such as SnO_2. These paramagnetic species, however, cannot be observed under operando conditions (under oxygen exposure and at the operating temperatures of sensors).[136,137] Hence, powders or films are treated in situ (at operating temperature, under gas exposure), but the spectra are recorded at −196 °C or room temperature after evacuation and rapid quenching of the samples. The most-cited paper on the in situ EPR study of oxygen interaction with SnO_2 (by Chang[184]) is inconsistent with other EPR studies and appears to involve a misinterpretation of EPR results (for details, see our recent review[89]).

5.6. On-Line and Off-Line Gas Analysis

The first experimental attempt to deduce the sensing mechanism by correlating the change in the conductance of metal oxides with their catalytic activity dates from 1978.[140] The mechanism of CO detection on Co_3O_4 was addressed by a combination of catalytic conversion (on powders) and conductance (on films) measurements. Gases were analyzed before entering the reactor and after leaving the reactor by chromatography. In 1989, Kohl[91] reviewed the surface reactions and electronic response of SnO_2 gas sensors exposed to a certain dose of CH_3COOH, CO, or CH_4. In these studies, an improved mass-spectrometry technique, reactive scattering of a molecular beam, was applied under UHV conditions at the sensor surface at working temperature with the simultaneous monitoring of the surface conductivity.

Subsequently, much effort has been made to correlate the catalytic activity (as "combustion" or "conversion") obtained through on-line or off-line analysis of the reaction products with the sensor activity. On-line gas analysis was performed by mass spectrometry,[91,185–187] by gas-phase FTIR or PAS (photoacoustic spectroscopy),[169,170,188,189] by using gas sensors (e.g. electrochemical oxygen sensors or capacitive humidity analyzers),[146,190] or specific gas analyzers (NOx chemiluminescence analyzer and ozone UV analyzer).[191]

To overcome the sensitivity limitations caused by the small amount of sensing material, a setup for "consumption" measurements was proposed in which one sensor mounted in a separate chamber upstream of the others monitored sensor activity, while six to ten further sensors in another chamber measured the "catalytic conversion" (Figure 13). The composition of the gas was monitored simultaneously upstream and downstream of the sensors along with resistance measurements.[189,190]

Off-line gas analysis was also performed by: 1) the condensation of large quantities of stream gases and subsequent analysis by NMR spectroscopy, and 2) headspace analysis of a small static volume with GC–MS.[192]

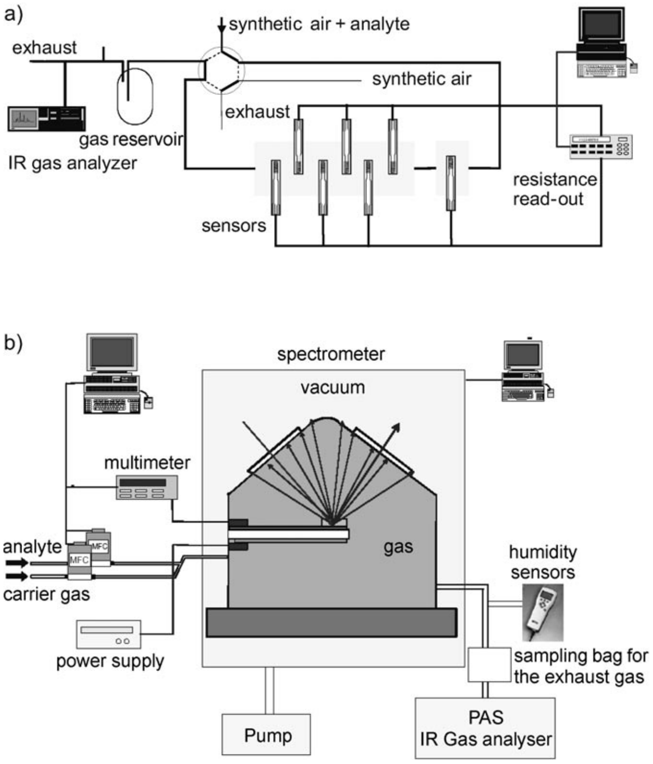

Figure 13. On-line gas analysis. a) Setup for consumption measurements: several sensors are used for increased consumption and to allow switching between incoming and outgoing gas streams.[189] b) Setup for simultaneous DRIFTS investigations, electrical measurements, and on-line gas analysis on a sensor.[169,170]

6. Correlation of Sensor Activity with Spectroscopic Data

The spectroscopic data from operando or in situ investigations must be correlated with the sensor activity, expressed as either sensor response or a sensor signal. This comparison can be done for either steady-state (Figure 14a,b) or transient conditions; the latter requires time-resolved spectroscopy (Figure 14c,d). We will address several representative examples of in situ and operando spectroscopic investigations of the interaction of oxygen, water, and CO ("detection") with different metal-oxide sensors (e.g., SnO_2, Ga_2O_3). Table 5 gives a short summary of other model studies.

A number of spectroscopic studies of the interactions of oxygen and water with metal-oxide gas sensors because of their use under real-world conditions (atmospheric pressure, ca. 20.5 vol% O_2 (corresponding roughly to that in air), ca. 1.5 vol% H_2O (50% relative humidity (RH) at 20 °C)) form the basis of the mechanistic description of gas sensing on metal-oxide sensors. Studies of the mechanism of CO detection in air or nitrogen represent a third important aspect of the characterization.

We give two examples of typical measurement approaches: 1) simultaneous IRES and DC conductance studies of the interaction of water with a Ga_2O_3 sensor as an example of an operando approach (Figure 14)[167,171]), and 2) Mössbauer[35] and EPR[207] studies as typical "quenching" approaches (Figure 15).

1) Operando approach: Figure 14a shows the temperature dependence of Ga_2O_3 emission spectra during H_2O adsorption. The bands observed in the IRES spectra were attributed to adsorbed molecular water (3476 cm^{-1} and a broad band at 1700–3700 cm^{-1}) and the stretching vibration of single and bridging OH groups (3720 and 3653 cm^{-1}, respectively). The integrated areas of the emission spectra (Figure 14b) showed that the number of bridging OH groups increased with temperature, whereas the band areas related to adsorbed molecular water and single OH groups decreased. These changes were correlated with the observed changes in the sensor signal and explained by several competitive effects:[167,171]

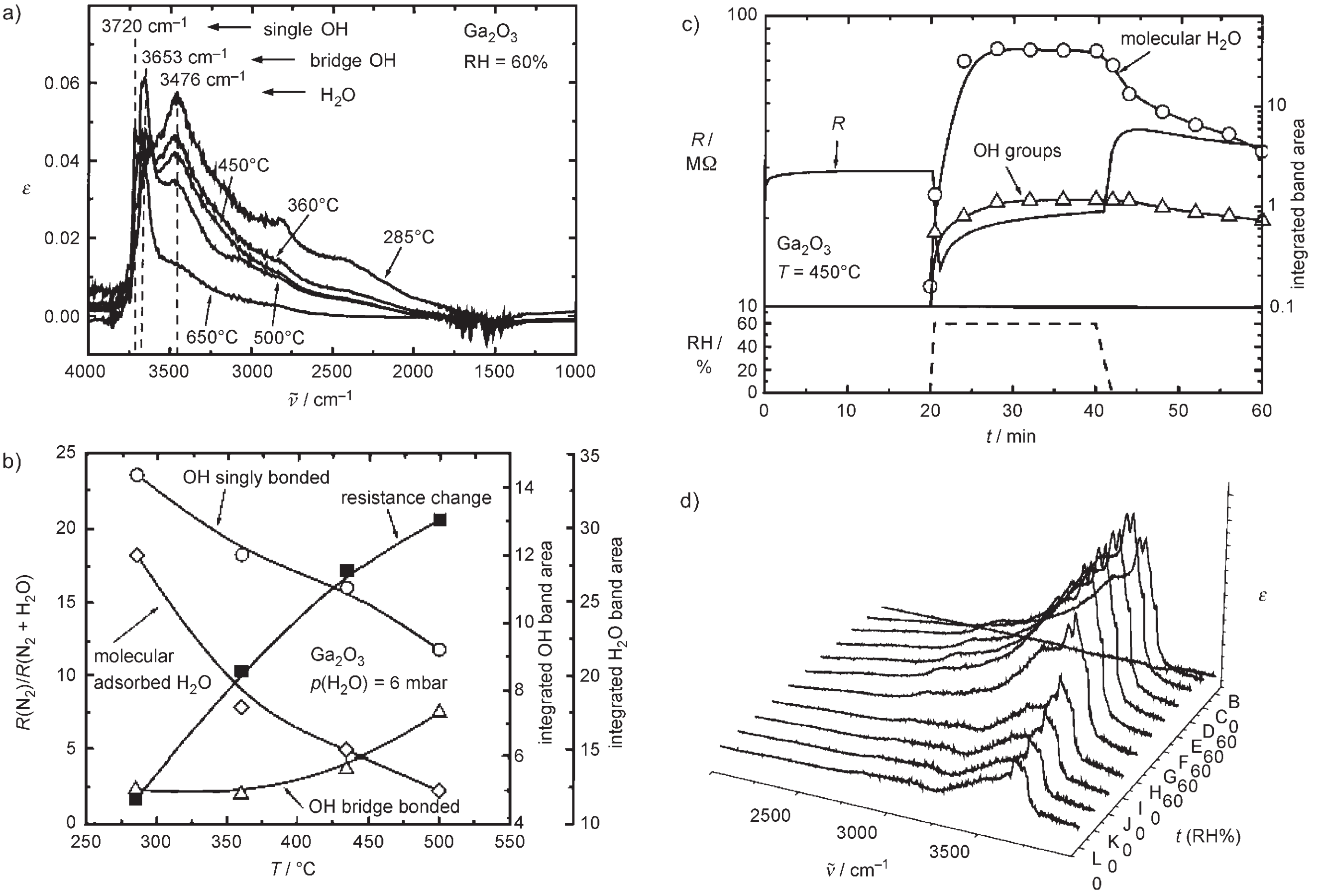

Figure 14. Results of operando IRES study and dc resistance measurements of the interaction of H_2O with Ga_2O_3 sensors:[167,171] a) Emission spectra, b) resistance changes and integrated band areas, c) changes of the resistance and integrated band area in dry air upon a humidity pulse of 15% RH, and d) time-resolved spectra of the sensors exposed to 60% RH at 450 °C. See text for details.

a) The ionosorption of water and partial charge transfer from adsorbed molecular water results in a decrease in the sensor resistance [Eq. (1)].

$$H_2O_{(gas)} \rightarrow H_2O_{(ads)} \rightarrow H_2O_{(ads)}{}^{\delta+} + \delta e^- H_{(ads)} \quad (1)$$

b) Water vapor reacts with lattice oxygen to give two types of surface hydroxy groups [Eqs. (2) and (3)].

$$H_2O_{(ads)} \rightarrow OH_{(ads)} + H_{(ads)} \quad (2)$$

$$H_{(ads)} + O_{(lat)} \rightarrow V_O{-}OH_{(ads)} \quad (3)$$

c) Water reacts with ionosorbed surface oxygen [Eq. (4)].

$$H_{(ads)} + O_{(ads)} \rightarrow OH_{(ads)} \quad (4)$$

d) Ionosorption of hydroxy groups results in an increase in the resistance [Eq. (5)].

$$\delta e^- + OH_{(ads)} \rightarrow OH_{(ads)}{}^{\delta-} \quad (5)$$

Evaluation of the time-resolved spectra (Figure 14c, d) and the simultaneously recorded electrical resistance revealed that the exposure to water vapor results in a rapid decrease in resistance, which was described by the adsorption of molecular water [Eq. (1)]. In a second step, the resistance increased much more slowly as a result of ionosorption of OH groups [Eq. (5)]. Similar behavior was observed when the water injection was stopped: after a rapid increase in resistance caused by the desorption of water, the resistance decreased slowly, which was attributed to the dehydroxylation of the surface. This mechanistic description cannot unfortunately give convincing evidence for either of the two models of gas sensing.

b) In situ (quenching) approach: Figure 15a, b shows the changes in electrical response with a change in Sn^{II} concentration, measured by in situ Mössbauer spectroscopy for nanocrystalline SnO_2 in the presence of CO and dry air at 380 °C. The conductance changes concomitantly with the change of the tin oxidation state (which in turn indicates the formation of oxygen vacancies).[96] A rapid and pronounced increase in Sn^{II} concentration was observed just after admission of CO into the reactor. The Sn^{II} component disappeared 1 min after the admission of air. A very low concentration of Sn^{II} (1 mol%) was sufficient for the conductance to change 1000-fold, and a further increase of Sn^{II}

Table 5: In situ and operando case studies of gas sensing on semiconducting metal oxides.

Approach	Methods	Oxides	Gases	Main findings
operando	IRES	Ga_2O_3[171]	1) H_2O, 2) C_2H_4, acetone, ethanol	1) molecular and dissociative water ionosorption; 2) full oxidation of organic molecules; molecularly adsorbed water at the surface
		WO_3, $AlVO_4$ and Co_3O_4[99]	O_2 in N_2, C_3H_6 and acetone in air	ionization of oxygen vacancies
	DRIFTS	SnO_2[170, 193]	1) O_2 and H_2O in N_2 2) propane in dry/wet air	1) water dissociation mediated by ionosorbed oxygen; 2) reaction of propane with ionosorbed oxygen
		Pd/SnO_2[168]	CO/dry and humid air	role of surface hydroxy groups in CO oxidation; CO reaction with ionosorbed oxygen
		CdGeON[28, 166]	O_2 in N_2	filling of oxygen vacancies; change of the Ge coordination number
	XAS	SnO_2 and Pd/SnO_2[176, 194]	CO and H_2 in N_2	Sn^{4+} and Pd^{2+} reduction as secondary processes, CO and H_2 oxidation by ionosorbed oxygen
	XAS	Pt/SnO_2[175]	CO in N_2, H_2S	variation in Pt oxidation state in reducing and oxidizing atmospheres
parallel-sensors	XAS	SnO_2; Pt/SnO_2[173, 174]	air, CO/air, CO/N_2, O_2	variation in Pt oxidation state in reducing and oxidizing atmospheres
	CEMS	Bi_2O_3-SnO_2[178, 179]	He, CO/He, CH_4/He	oxidation by lattice oxygen atoms, formation of oxygen vacancies
	CEMS	α- and γ-Fe_2O_3[143]	CO_2/He, i-C_4H_{10}/He	reduction of γ-Fe_2O_3 to Fe_3O_4
operando-pellets	FTIR-T	TiO_2, SnO_2, In_2O_3, WO_3[162, 172, 195–198]	CO_2, CO, O_2, O_3, NO_x	variations of the free carriers density
	FTIR-T	SnO_2[161]	air, CO, H_2O	oxygen adsorption on defective dehydroxylated surface
	Raman	WO_3[165]	dry air, 10% CH_4/H_2, 1.8% CO/N_2, NO_2/N_2	oxidation of active carbon formed at the surface through catalytic cracking of CH_4
		CuO-SnO_2 ; SnO_2[163, 164]	dry air, H_2S/Ar	formation of Cu_2S or SnS_x
parallel	FTIR	SnO_2[98, 199]	O_2/N_2, CO/air, He/air	photoionization of ionized oxygen vacancy with increasing oxygen content
		SnO_2, MoO_x-SnO_2, Pd/SnO_2, WO_x-SnO_2[200–204]	O_2, CO, NO, NO_2	formation of oxygen vacancies and their ionization
	DRIFTS	Cr-doped WO_3[205]	air, NH_3	NH_3 reaction with W=O centers, reduction of W atoms
	DR UV/Vis	SnO_2[206]	O_2, hydrazine	formation of oxygen vacancies and their ionization
parallel-quenching	CEMS	SnO_2 and Ru, Pt, Pt/SnO_2[207, 208]	NO/argon, air	formation of oxygen vacancies and their ionization
		SnO_2 and Pd/SnO_2[35]	CO/N_2, air	formation of Sn^{II} as an indicator of oxygen-vacancy formation
	EPR	SnO_2; Ru, Pt, Pt/SnO_2[96, 207–209]	dry and humid air, CO in air and N_2, NO/Ar, H_2	formation of oxygen vacancies and their ionization
	DR UV/Vis	MoO_3, WO_3, and MoO_3-WO_3,[97, 182] Cr_2O_3-SnO_2[183]	O_2, CO/O_2, NO_2/O_2, ethanol, NH_3	electronic transitions related to oxygen defects

concentration up to 14 mol% under exposure to CO did not significantly change the conductance.

Figure 15 c,d shows the EPR spectroscopic investigation of the mechanism of NO detection on SnO_2 samples. No paramagnetic species were observed in the SnO_2 samples annealed in air. Samples treated with a flow of NO/Ar showed symmetrical resonance lines at $g = 1.890$, which were attributed to electrons trapped in singly ionized oxygen vacancies ($V_O^{\bullet}$). Accordingly, the mechanism of NO detection was attributed to the reaction of NO with oxygen in the lattice [Eqs. (6) and (7)].[207]

$$NO_{(gas)} + O_{O(lat)} \rightarrow NO_2{}^-{}_{(ads)} + e^-(CB) \tag{6}$$

$$NO_2{}^-{}_{(ads)} \rightleftharpoons NO_{2(gas)} + V_O^{\bullet} \tag{7}$$

The number of these paramagnetic defects was calculated to be about 10^{16} spin g^{-1}, and increased with increasing temperature of the NO treatment. If samples were subsequently treated in air stream at 25 °C, the intensity of $V_O^{\bullet}$ resonances decreased significantly, and the spectrum showed, besides residual $V_O^{\bullet}$ signals, new resonances at $g_1 = 2.023$, $g_2 = 2.005$, $g_3 = 1.999$, which are typical of $Sn_{Sn}O_2^-$ centers [Eqs. (8), (9)].

$$O_{2(gas)} + V_O^{\bullet} + Sn_{Sn}{}^{\times} \rightleftharpoons Sn_{Sn}{}^{\times}{-}O_2{}^- + V_O^{\bullet\bullet} \tag{8}$$

$$O_{2(gas)} + e^-(CB) + Sn_{Sn}{}^{\times} \rightleftharpoons Sn_{Sn}{}^{\times}{-}O_2{}^- \tag{9}$$

The decrease in the resistance values in the thin films correlated with the appearance as well as with the concentration of $V_O^{\bullet}$ defects in powder samples.[207]

In many cases, however, such a simple correlation between sensor activity and spectroscopic data is not observed. Moreover, sometimes the spectroscopy as well as on-line gas analysis seems to represent only secondary processes that are not responsible for the sensing. We will give two examples, one for operando XAS data and the other

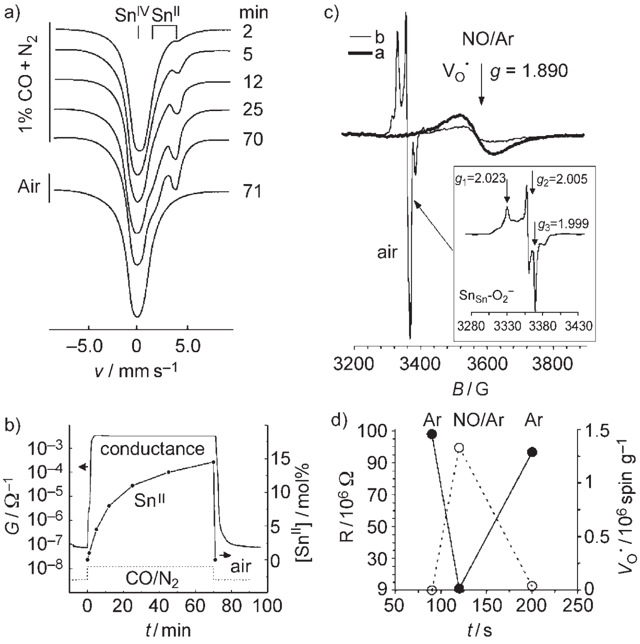

Figure 15. a) Mössbauer spectra of SnO$_2$ in 1% CO/N$_2$ and then in dry air at 380 °C.[35] b) Electrical response of SnO$_2$ and change of Sn^{II} concentration in 1% CO/N$_2$ and dry air at 380 °C with a gas flow rate of 4 L h^{-1}.[35] c) EPR spectra showing $V_O^{\bullet}$ defects (line a) and Sn$_{Sn}$-O$_2^-$ centers (line b). The inset shows a magnification of the resonances of the Sn$_{Sn}$-O$_2^-$ centers. d) Resistance values in thin films (●, left axis) and $V_O^{\bullet}$ defects concentration (○, right axis) in powder samples at 350 °C.[207] See text for details.

a typical problem with on-line gas analysis. Figure 16 a, b[176] shows the correlation between the electrical conductance and the oxidation states of Pd and Sn during cycling of a Pd-SnO$_2$ film in H$_2$ and O$_2$ gas mixtures. At 100 °C, the conductance changes without variation of the Pd and Sn oxidation states. At higher temperatures, the oxidation state of Pd varies considerably depending on the atmospheric composition. However, there is no direct correlation between the conductance and the oxidation states of Pd and Sn; even at 300 °C, the conductance changes by several orders of magnitude without any measurable variation of the oxidation states of both metals. These results indicate that oxidation and reduction of Pd nanoparticles and the SnO$_2$ matrix are the secondary processes that are not responsible for the sensitivity to H$_2$.

Moreover, the sensor activity is not always correlated with the results of the on-line gas analysis (see, for example, references [170,189,210–212]). Figure 16 c, d shows the correlation between the sensor signal and the consumption of different gases according to on-line gas analysis: At 200 °C, the sensor shows relatively high activity for propane detection (signal of 6–400 ppm). The combustion, however, is almost negligible.[189] The same also holds for higher temperatures and other analytes. Other studies have also demonstrated no direct correlation between sensor response for materials such as SnO$_2$ and TiO$_2$ and the production of CO$_2$ (a measure of catalytic activity).[188,211,212]

The examples given above show that the operando and in situ spectroscopy provide evidence for and against both

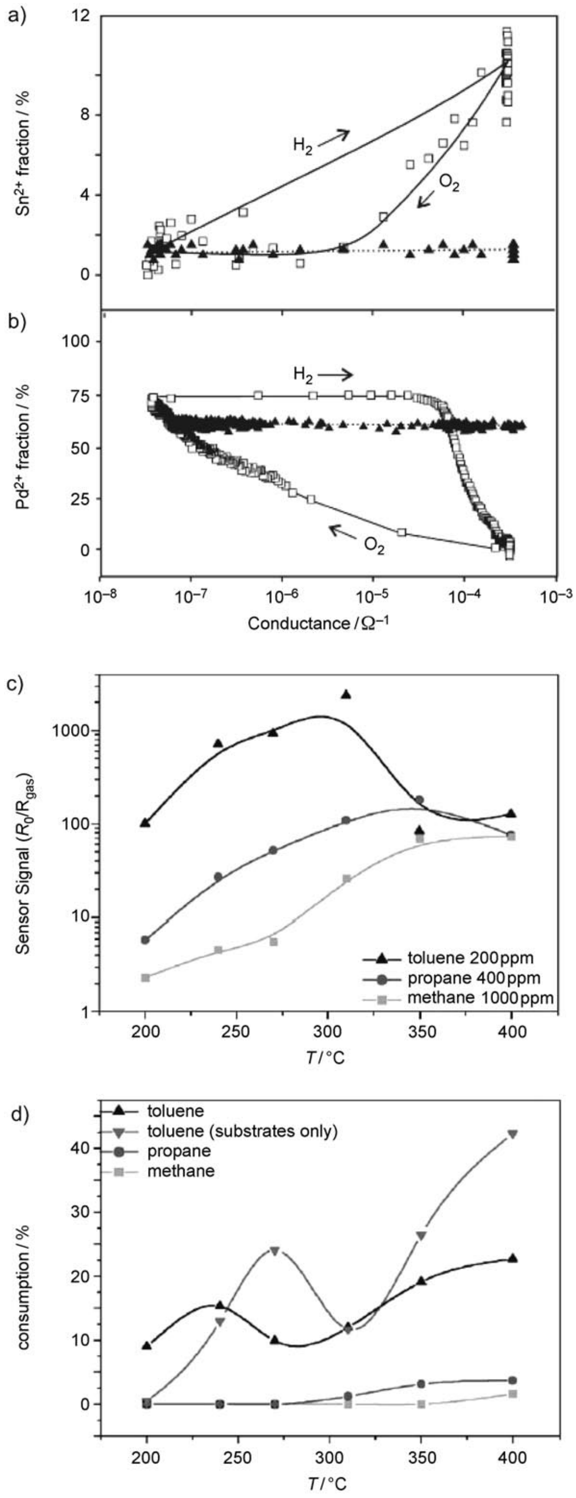

Figure 16. Secondary processes that are not responsible for the sensing. a,b) Operando XAS and conductance studies. The correlation between the conductance of a Pd-SnO$_2$ film and the oxidation states of tin (a) and palladium (b) at 300 °C (□, -----) and 100 °C (▲, •••••). Pd^{2+} fraction is the concentration of Pd^{2+} in the Pd^{2+}/Pd^0 mixtures; Sn^{2+} fraction is the concentration of Sn^{2+} in the Sn^{2+}/Sn^{4+} mixture. The arrows indicate the direction in which the system changes during exposure to H$_2$ and O$_2$.[176] c,d) On-line gas analysis. c) Sensor signal of SnO$_2$ sensors exposed to different analytes in dry air dependent on operating temperature of the sensors, and d) overall gas combustion measured by on-line PAS.[189] See text for details.

models of gas sensing (ionosorption and oxygen-vacancy models). The interpretation of the spectroscopic data therefore depends on the mechanistic model chosen a priori.

Ionosorbed oxygen has never been observed in operando and in situ studies of metal-oxide sensors under working conditions.[98,99] By contrast, operando and in situ spectroscopy provides very strong evidence for the reaction and ionization of oxygen vacancies in working sensors.[35,96–99] In situ FTIR studies[98,199] of SnO_2 under working conditions (at 375 °C and 450 °C) showed an increase in the intensity of a broad band in the region 2300–800 cm^{-1} (X-band) with increasing oxygen content. The position of the adsorption edge near the ionization energy of the second-highest level of oxygen vacancies (1400–1500 cm^{-1}, 170–180 meV) points to an electronic transition from this level to the conduction band (photoionization of $V_O^{\bullet}$ to $V_O^{\bullet\bullet}$).[204] Accordingly, this band can serve as an indicator of the electron concentration in the neighborhood of oxygen vacancies in SnO_2. Similar effects were observed on Ga_2O_3, $AlVO_4$, and WO_3.[99] However, this interpretation appears to contradict early electrophysical measurements on SnO_2,[169] which showed that the donor levels in SnO_2 are located at around 30 and 150 meV below the conduction band and will be completely ionized at the sensor operating temperatures.[213,214]

The indirect spectroscopic evidence of adsorbed oxygen[193] can also be explained and treated within the framework of both models. For example, it was found that oxygen promotes water vapor dissociation on SnO_2 at 330–400 °C:[193] the concentration of hydroxy groups (peaks at 3640 cm^{-1}) increased at low concentrations of oxygen (2000 ppm) and water vapor (3 ppm) and tended towards saturation. This effect was explained by the reaction in Equation (10).

$$H_2O_{(gas)} + O^-{}_{(ads)} + 2\,Sn_{Sn}{}^{\times} \rightleftharpoons 2(Sn_{Sn}{}^{\times}{-}OH) + e^-(CB) \tag{10}$$

At first sight, this reaction seems to be evidence for the ionosorption model. However, the increase in concentration of the hydroxy groups upon oxygen exposure can be explained also by completely different processes within the framework of the oxygen-vacancy model. For example, an EPR signal of singly ionized oxygen vacancies ($V_O^{\bullet}$) at $g =$ 1.89 was observed after treatment of SnO_2 with wet air at 200 °C.[215] The influence of water and oxygen can be described by Equations (11) and (12).

$$H_2O_{(gas)} + 2\,Sn_{Sn}{}^{\times} + O_O{}^{\times} \rightleftharpoons 2(Sn_{Sn}{}^{\times}{-}OH) + V_O{}^{\bullet} + e^-(CB) \tag{11}$$

$$2\,V_O{}^{\bullet} + O_{2(gas)} + 2\,e^-(CB) \rightleftharpoons 2\,O_O{}^{\times} \tag{12}$$

These examples clearly show that the current models of gas sensing on metal oxides cannot explain all the effects observed on operating metal-oxide sensors. This goal will only be achieved by the combination of operando spectroscopic and electrical characterization techniques.

7. Mechanism of Catalytic Reactions: Insights from Electrical Measurements?

Can electrical techniques such as dc conductance or ac impedance spectroscopy help to clarify the mechanism of catalytic or photocatalytic reactions? Unfortunately, answer to this question is not a simple "yes" or "no". These methods are restricted to (semi-)conducting materials and to the catalytic reactions that involve free charge carriers (electrons and holes in electronic materials; ions in ionic and mixed conductors[216]). Nevertheless, in situ electrical monitoring offers considerable scope for studying catalysts under operating conditions (review in reference [217], see also references [218,219]). It provides information about the mechanism of the charge transfer between the catalyst and adsorbed species—and thus about the entire catalytic reaction—and can monitor processes at the surface and in the bulk of a catalyst, thus providing information about the initial stages of poisoning and deactivation.

The first possible application is found in the mechanistic studies of photocatalysis on semiconducting (n-type) TiO_2. The dc conductance as well as work function change measurements can provide a method—complimentary to EPR[220,221] and IR[222,223] spectroscopy—for the investigation of photochemistry on TiO_2 because charge transfer to adsorbate molecules involves both Ti^{3+} sites and the conduction-band electrons.[222,223]

The second area of application is the study of oxidation processes in which electrons are transferred between reacting molecules and a solid-oxide catalyst. Within the framework of the electronic theory of catalysis, the lattice defects can serve as centers of localization of conduction electrons (or holes) and act as surface donor or acceptor levels within the band gap. They also mediate the transfer of electrons between the solid and the adsorbed molecules, which is the rate-determining step of the oxidation process (e.g., for the breaking of a C–H bond).[224]

A third possible application is the study of deactivation phenomena such as sintering, poisoning, phase changes, or solid-state reactions between components. The electrical techniques offer very sensitive and relatively simple methods of studying these processes under realistic conditions.[217,219]

Herein we face also a historical link between heterogeneous catalysis and gas sensing. As already mentioned above, the current models of gas sensing originate formally from the electronic theory of catalysis[42–44] and, in particular, from the boundary layer theory of chemisorption.[45,46] Electron exchange between catalysts and gaseous initial, intermediate, and end species is frequently decisive in heterogeneous catalysis, so new methods for the determination of Fermi potentials and space–charge phenomena in catalysts as well as the measurement of work functions and charge transfer levels will offer further insight into the mechanisms of catalysis.[60] Electrical techniques have been used not only as another characterization method for the catalyst,[225,226] but also for studying the mechanism of catalytic reactions in situ. Different techniques for measurement of work-function changes and surface potentials as well as semi- and photoconductivity were surveyed in one of the first monographs on the experimental methods in catalytic research.[227] From the changes in surface potential and work function, for example, dipole moments of adsorbed molecules were obtained, and conductivity measurements served as a simple and sensitive tool to follow adsorption much more accurately than by direct volumetric measurement.[40]

The results of numerous electrical studies over more than 60 years on metal oxides can be found in many reviews and books (see, for example, references [41,43,44,48–50,112] and references therein). In light of these activities, it is remarkable to read recent statements that "there have as yet been no studies on the effect of the conducting or defect properties of the catalysts on their catalytic behavior"[228] and that there is "an urgent need for better knowledge concerning the relation between the conducting properties of the bulk and of the surface region […] to obtain a fuller understanding of the connection between these properties and the catalytic behavior."[216]

8. Summary and Outlook

The present models of gas sensing cannot explain all the effects that are observed on operating metal-oxide-based sensors. Further progress requires a mechanistic description that is based on a combination of experimental methods and the theoretical modeling studies. For this purpose, a methodology is required that allows the physicochemical processes that occur on an active sensing element to be monitored in real time and under operating conditions. Hence, the improvement of the in situ spectroscopic tools and its combination with electrical characterization is of primary concern to future research activities. Also of importance is the development of quantum-chemical methods that allow the prediction of surface structure and reactivity of metal-oxide-based sensors in terms of temperature, pressure, and composition of the gas-phase.

In this way, the physicochemical processes on an active sensing element under working conditions could be clarified and new insights could be gained into the mechanism of gas–solid interactions. The potential of these methods, however, is not yet fully recognized. In the coming years, one can expect real breakthroughs in terms of mechanistic understanding, theoretical advances, and methodological developments.

8.1. Problems of Particular Importance for the Mechanistic Description of Gas Sensing

In situ and operando spectroscopy can greatly contribute to answering several questions about the mechanistic description of gas sensing.

8.1.1. The Role of the Electrodes

The material of the sensing electrodes plays a significant role in the overall sensor performance: for example, Pt gives a much higher sensor signal than Au for CO.[149] This difference is thought to be caused by the catalytic activity of the electrode material. It was also suggested recently that the interface between the electrode and the sensing layer activates gaseous oxygen and thus increases the sensing activity.[229] However, this effect has never been proved experimentally. In contrast, the kinetics studies showed that CO is activated on Pt, but oxygen is activated on SnO_2.[230] Simultaneous XAS (EXAFS, XANES) and conductance investigations could help to solve this contentious question.

8.1.2. Spectroscopic Evidence for Adsorbed Oxygen Species on Sensors under Operating Conditions.

This is one of the most difficult and most important problems in gas sensing: According to the ionosorption model (Section 2.3.1), oxygen adsorbs at the oxide surface in a delocalized manner, trapping electrons from the conduction band and forming ions—charged molecular ($O_2{}^-{}_{ads}$) and atomic ($O^-{}_{ads}$ and $O^{2-}{}_{ads}$) species—that are electrostatically stabilized at the surface in the vicinity of metal cations. This process is suggested to occur under real sensor working conditions, namely, at 100–450 °C under atmospheric pressure and with 20.5 vol % oxygen, but, despite many endeavors, there is not yet any convincing spectroscopic evidence for it. Neither the superoxide ion $O_2{}^-$, nor charged atomic oxygen O^-, nor the peroxide ion $O_2{}^{2-}$ has been observed on SnO_2 under real working conditions.[89] Any spectroscopic evidence and theoretical modeling results—either for or against this mechanism—will greatly advance the basic understanding of gas sensing.

8.1.3. Oxygen Vacancies

The role of oxygen vacancies can be addressed in model studies of the mechanism of CO detection in the presence and in the absence of oxygen. Within the framework of the ionosorption model, CO acts as an electron donor in an oxygen-free atmosphere (and when the surface is free of adsorbed oxygen) and is adsorbed as CO^+ by inserting an electron into the conduction band. Within the framework of the reduction–reoxidation mechanism (oxygen-vacancy model), CO removes oxygen from the surface of the lattice to give CO_2, thereby producing an oxygen vacancy. The contradictions between the results from the kinetics[132,230] and the spectroscopic[35,96,173,174] studies on SnO_2 and the results of sensor investigations[210,211,231] could be resolved by even a relatively simple operando experiment that compared sensor activity with reaction products ("CO_2"), degree of surface reduction (number of oxygen vacancies), and the adsorbed species (CO, CO^+, carbonates, and carboxylates). However, in such an experiment, the roles of the interfaces (heater, electrodes, sensing material) and limitations caused by the low amount of sensing material would need to be addressed.

8.2. Theoretical Advances

Until now, quantum-chemical calculations of the interaction of gas with metal-oxide-based sensors (e.g., SnO_2) have been done only for zero-temperature and zero-pressure

Table 6: Development possibilities for operando and in situ methods for study of the gas-sensing mechanism.

Method	Current status	Possible operando studies
FTIR (transmission)	operando-pellets	↑operando
DRIFTS	operando	=
IRES	operando	=
Raman	–	↑operando
DR-UV/Vis	parallel-quenching	↑operando
CEMS	parallel-sensors[1)]	↑operando
EPR	parallel-quenching	↑parallel-sensors
XAS	operando	=
NMR	–	↑parallel-sensors

↑: potential for development.

conditions (see, for example, references [89,127] and references therein). However, these methods (a combination of ab initio calculations with thermodynamic models) can now be used to calculate the surface structure and reactivity of metal oxides in terms of temperature, pressure, and composition of the gas phase[232,233] and to determine the equilibrium composition and geometry of a surface in contact with a given environment at finite temperature and pressure.[234,235] They can be also used to simulate the adsorption of molecules to surfaces under working conditions, thus allowing a direct comparison with experimental data (e.g. from the vibrational spectroscopy) obtained in situ.

Application of these theoretical methods to gas-sensing problems will contribute to a better description of the mechanism of gas sensing as well as advance the fundamental understanding of gas–solid interactions.

8.3. Methodological Development

The general trends in the field of operando and in situ characterization of catalysts include: 1) the combination of multiple techniques to add “a third dimension to operando spectroscopy”,[236,237] and 2) the development of methods to sense and spectroscopically observe single molecules (for example, with “reporter molecules”;[238] see also references [13,239]). This approach is, however, even more challenging with gas sensors; a shorter-term goal would be the further adaptation of spectroscopic techniques and cells for in situ and operando studies (Table 6).

For example, in situ MAS solid-state NMR spectroscopy under flow conditions (MAS = magic angle spinning)[240,241] will provide useful information about the detection of organic molecules. Figure 17 a shows the mechanism of C_2H_5OH detection on SnO_2 sensors proposed more than 15 years ago,[91] but never confirmed experimentally under realistic conditions. This mechanism assumed the formation of surface ethoxy groups and their transformation into acetaldehyde as a key step in the detection of ethanol on

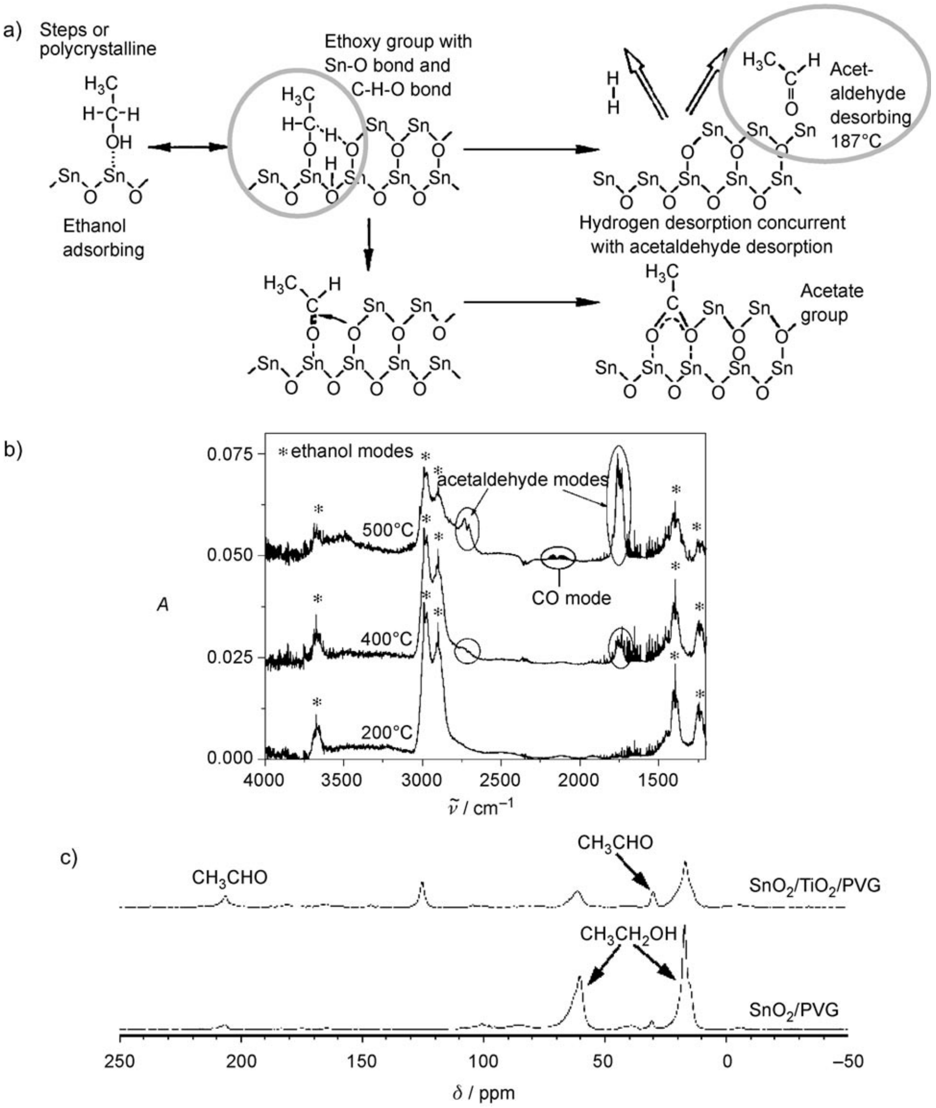

Figure 17. Use of NMR spectroscopy for in situ studies of the gas-sensing mechanism: a) proposed mechanism of C_2H_5OH detection on SnO_2 sensors,[91] b) gas FTIR spectra during detection of ethanol on SnO_2,[183] and c) proton-decoupled ^{13}C Bloch decay spectra acquired after in situ UV irradiation for 315 min on $SnO_2/TiO_2/PVG$ (top) and SnO_2/PVG (bottom); PVG: porous vycor glass.[242]

SnO_2. The formation of acetaldehyde was confirmed by FTIR spectroscopy by following the changes in the gas-phase spectrum (Figure 17b[183]). However, no vibrational modes for chemisorbed species could be detected. What happens, however, on the surface? The section of a $^1H,^{13}C$ CP/MAS NMR spectrum of UV-treated SnO_2 in EtOH (Figure 17c)[242] clearly demonstrates the possibility of clarifying the mechanism of ethanol detection on SnO_2. In the subsequent $^{13}C,^{119}Sn$ REDOR studies, the formation of ethoxide on SnO_2 ($^{119}Sn{-}O^{13}CH_2CH_3$) through the interaction with ethanol was confirmed. Other possible methods include ^{119}Sn and ^{17}O MAS NMR spectroscopy.[243] Accordingly, it is only a question of time until in situ MAS NMR spectroscopy will be applied for gas-sensing studies.

The combination of spectroscopic and electrical characterization techniques will bring fundamental and groundbreaking insights into gas-sensing mechanisms and thus lead to the development of better sensors. However, research activities will not stop there: The "life cycle" of a sensors includes preparation, activation, operation with deactivation, and, when possible, regeneration. Understanding the reactions and conductance mechanisms involved is only a part of the total understanding of a sensor.[91]

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