Materials for Chemical Sensing

Subjects: Physics, Applied

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The ability to measure and monitor the concentration of specific chemical and/or gaseous species (i.e., “analytes”) is the main requirement in many fields, including industrial processes, medical applications, and workplace safety management. As a consequence, several kinds of sensors have been developed in the modern era according to some practical guidelines that regard the characteristics of the active (sensing) materials on which the sensor devices are based. These characteristics include the cost-effectiveness of the materials’ manufacturing, the sensitivity to analytes, the material stability, and the possibility of exploiting them for low-cost and portable devices. Consequently, many gas sensors employ well-defined transduction methods, the most popular being the oxidation (or reduction) of the analyte in an electrochemical reactor, optical techniques, and chemiresistive responses to gas adsorption. Many of the efforts devoted to improving these methods have been directed towards the use of certain classes of specific materials.

gas sensors ionic liquids metal–organic frameworks MOF-based composites optical sensors chemiresistors electrochemical sensors oxygen hydrogen chemical sensing

1. Introduction

It is widely recognized that the development of technologies suitable for the identification and measurement of concentration of gaseous species is of great significance in many fields, including, for example, public health and safety, energy, climate, and environmental risk assessment. While it is clear that useful sensing devices (also referred to as “sensors”) must fulfill analytical standards, it is important to underline that other additional requirements exist, whose relative importance may vary depending on the specific application. Here, researchers can mention, for example: low production and consumption costs, small sizes, device portability for in-field measurements, possibility to transmit the data remotely, and so forth. A couple of examples of public documents available on the web are given here [1][2] as references for the economic figures involved.

The need to monitor the concentration of several kinds of gases (“analytes”) is recurring or, more appropriately, constantly present in many industrial processes, medical activities and everyday life activities. Due to this, several kinds of gas-sensing devices—based on different technologies and on different gas-sensitive materials—have been developed in the modern era [3][4][5][6][7][8][9]. Hence, a review on gas sensors and on the related technologies can be organized in different ways, such as by focusing on the transduction technology, on the specific application in which given sensors are employed, on the analyte to be revealed or, finally, on the active materials which allow sensing the gas molecules.

The present entry is organized according to the latter criterion and is structured in sections dedicated to different typologies of materials. In particular, researchers review here some more recent developments in the use of ionic liquids and metal–organic frameworks (MOFs) in chemical sensing. Regarding the latter class of materials, the present entry considers both MOFs used in pure form and, more extensively, composite materials in which a MOF is a component of the active sensing materials. In more detail, researchers will discuss hybrid materials in which MOFs are integrated with metal oxides, carbon-based materials, metal nanoparticles, and conducting polymers.

For the sake of clarity, researchers will first spend the first part of this introduction by pointing out (i) some of the applications requiring the use of chemical sensors and gas sensors, (ii) some of the most important analytes which are extensively considered in the present entry, and (iii) the physical/chemical mechanisms for the detection and concentration measurements of the gaseous species which are at the basis of the kind of sensors considered in this work.

Among the most important fields that involve or require gas sensing and concentration measurements, researchers shall mention at least: (i) environmental monitoring, which includes, for example, the control of indoor air quality [6][10][11] and the analysis of air pollution caused by vehicular traffic [12][13]; (ii) human safety, including the detection of harmful and/or explosive gases [14][15][16][17]; and (iii) medical application and diagnoses, such as breath and blood analysis [18][19]. A large variety of applications exist in reference to these fields, whose review is below the scope of the present work. It is worth mentioning that almost any (if not, any) monitoring activity has to be performed on-site and that measurements shall be collected in real time for various reasons (consider, for example, the case in which sensors have to monitor an industrial process or the leakage of some toxic species in an enclosed area). Moreover, prolonged monitoring is very often also needed, so the cost-effectiveness of running the sensor device is also an issue. This variety of applications and requirements explains why a wide array of sensing devices have been developed in recent decades [3][4][5][6][7][8][9][10][11][12][13][14][15][16][17][18][19][20][21][22][23][24][25][26].

The development of gas-sensing devices is in many cases focused on the detection of toxic or harmful gases generated by industrial processes or automobiles, such as NO and NO_2 (NO_x), CO, CO_2, SO_2, O_3, and NH_3. Other species to be mentioned are volatile organic compounds (VOCs), namely, organic compounds of small molecular mass which vaporize easily at room temperature such as acetone (CH_3CH_3CO), formaldehyde (HCHO), ethanol (CH_3CH_2OH), benzene (C_6H_6), toluene (C_7H_8), and others [16].

Molecular oxygen (O_2) is another analyte of importance. The possibility to detect it and to measure its partial pressure in air or, in most cases, when dissolved in some liquid medium (e.g., water or blood) is of paramount importance for many applications, such as medicine (e.g., the measurement of O_2 concentration in blood or in breath for medical diagnoses), plant biology, marine and freshwater research, and food technology and packaging. Several examples on the applications of O_2 sensing and extended references on the methods to achieve it are reported in excellent reviews [27][28][29].

The different physical/chemical mechanisms for the detection and concentration measurements of the gaseous species correspond, of course, to different classes/families of materials. However, gas-sensing materials shall ideally share some key characteristics, regardless of the transduction mechanism, the main and most obvious one being a large specific surface area (SSA). An exhaustive (although incomplete) list of possible approaches to gas sensing can be summarized as in **Table 1**.

Table 1. Types of sensor devices and their principle of operation.

Sensor Type	Examples	Principle of Operation
Electrochemical	Amperometric, ChemFET	Analyte molecules are involved in the redox reaction at the working electrode of an electrochemical cell, modulating the electrical current.
Electrical	Chemoresistors	Adsorbed molecules of the target gas interact with oxygen species adsorbed on the surface of a nanoparticulated semiconductor, modifying its charge depletion regions and its electrical conductivity.
Gravimetric	Surface acoustic waves, piezoelectric	A vibration resonance frequency is modified due to the adsorption of the target analyte. The shift in resonance frequency quantifies the analyte concentration.
Thermochemical	Catalytic bead sensors	The target gas is burnt, causing a temperature rise that changes the resistance of the detecting element of the sensor proportional to the concentration of combusted gas.
Optical	Absorptive Reflective Fluorescence-based	Adsorbed molecules of the target gas modify in several ways the optical properties of the sensing material (e.g., reflectivity, optical transmission, fluorescence spectrum and/or lifetime, etc.).

2. Ionic Liquids in Amperometric Gas Sensing—Recent Developments

Ionic liquids (ILs) are among the materials of interest for the development of improved amperometric gas sensors. Among their main characteristics, it is worth emphasizing their versatility, intended in reference to the broad range of the properties that they share [30][31][32].

Before discussing their applications, it is useful to sketch a general description of ILs. Generally speaking, ionic liquids are salts at the liquid state. However, the commonly used terminology restricts this definition, making a distinction between “room-temperature ILs” (also RTILs) which are liquid at room temperature and proper ILs, which are solid at room temperature but whose melting point is below 100 °C [33] or below some other conventional temperature larger than the room temperature. As evidenced by the name itself, ionic liquids are mostly made by ions, typically a small anion (either organic or inorganic) and a large organic cation. The type and the size of each of the ions determine the properties of a given ionic liquid. It can be generally stated that the cation affects the physical properties of the salt, while the anion affects its reactivity and chemical behavior. Some of these properties are specifically relevant for the case of interest, i.e., the use of ILs in amperometric sensing.

To begin with, researchers mentioned before that one major drawback of gas sensors based on electrochemical cells is that their usage is limited by the evaporation of the liquid electrolyte. This fact is one of the main drivers towards the use of ILs, as they are extremely nonvolatile. Other advantages of ILs include their intrinsic conductivity, high chemical stability, high viscosity, and wide electrochemical window. It is worth briefly discussing some of these properties.

Electrical conductivity and viscosity: The room temperature electrical conductivity of an ionic liquid is typically in the range of (about) 0.1–20 mS cm^{-1}. These conductivity values are smaller than those of common aqueous electrolyte solutions. This fact can be seen as a consequence of the relationship between the viscosity (η) and electrical conductivity (Λ) of an electrolyte solution, known as empirical Walden's rule, stating that their product is constant at a given temperature, i.e., $\Lambda\eta$=const. As this relation is empirically obeyed by both regular electrolyte solutions and ionic liquids [34], the viscosity is typically much larger in the latter with respect to the former. Typical values for η at room temperature range from 10 to 10^5 cP (centipoise) in ionic liquids, while values ranging from 0.1 to 10 cP are common for standard solvents. Considering the Walden's rule, the mentioned electrical conductivity values lower than those typical for aqueous solutions of standard electrolytes are explained. This point represents a major obstacle for applications, as the lesser electrical conductivity is accompanied by a lesser diffusion rate and by a decrease in the rate of reaction and separation processes.

Electrochemical window: The electrochemical window of a substance (e.g., a solvent) is, by definition, the electrode electric potential range between which the substance is neither oxidized nor reduced. It is important to determine the value of this quantity for both solvents and electrolytes when solutions are used in electrochemical applications. Large electrochemical windows of liquid solvents are favorable, as they allow the development of reactions involving solute molecules instead of unwanted reactions of the solvent. In the case of aqueous solution, the electrochemical window is about 1.23 eV, outside of which the electrolysis of water occurs. This value is regarded as relatively small. Conversely, the electrochemical window of ionic liquids is much larger, ranging from 4 to 5 volts typically, although higher values have been reported [35]. It is worth mentioning that the electrochemical window is sensibly affected by impurities in the ionic liquid, which have to be kept in control to avoid affecting the stability of the electrochemical cell.

The following **Table 2** reports some references on AGS using ILs as solvents, starting from the year 2016 and ordered by analyte.

Table 2. References on AGS using ionic liquids (ILs) as solvents, ordered by analyte.

Analyte	Ionic Liquid	Electrode	Analyte Concentration	Ref.
O_2				
	[C4mpyrr][NTf2]	Clark-type sensor with polycrystalline Pt gauze	1–20%	[36]

Analyte	Ionic Liquid	Electrode	Analyte Concentration	Ref.
	[C2mim][NTf2] and [C4mpyrr][NTf2]	Screen-printed (SP) electrodes	10–100% and 0.1–5%	[37]
	[N8,2,2,2][NTf2]	Pt MATFE	10–100%	[38]
	[C2mim][NTf2]	Pt microdisk and Pt MATFE	0.1–100%	[39]
	[MOmim][PF6]	Au microchannel electrode	5000–25,000 ppm	[40]
	[Bmim][BF4]	Au interdigitated electrodes	20–100%	[41]
	[C4mpyrr][NTf2]	Au on porous PTFE substrate	5–20%	[42]
	[C2mim][NTf2] and [C4mim][PF6]	SP electrodes (graphite)	0.1–20% and 100%	[43]
	[C4mpyrr][NTf2]	Au microchannel electrode	50–400 ppm and 2000–5000 ppm	[44]
	[C4mpyrr][NTf2]	Clark-type sensor with polycrystalline Pt gauze	5–20%	[45]
	[C4mpyrr][NTf2]	Interdigitated electrodes	1400–4800 ppm	[46]
	[C4mim][PF6], [C2mim][PF6] and [C5mim][PF6]	Pt interdigitated electrodes	0–100%	[47]
	[C4mim][BF4]	Planar electrodes	20–100%	[48]
	[Bmim][BF6]	Pt planar electrodes modified by NiCo2O4/rGO/[Bmim][BF6] composite	20–100%	[49]
	[C4mpn][Br]	Pt microelectrodes, 1% Ag-coated chitosan added to the IL	20–100%	[50]
	[Bmim][BF4]	SPE, solid polymer electrolyte (PTFE/Carbon nanotubes/IL)	2.1–12.6%	[51]
	[Emmim][TFSI] and [Bmim][TFSI]	Pt electrodes, IL + reduced graphene (rGO) + α-Fe_2O_3 electrolyte	20–100%	[52]
	[C2mim][NTf2]	IL membrane on Au-TFE	20–100%	[53]
	[C2mim][NTf2] added with	IL/poly(IL) membrane on Au-TFE	20–100%	[53]

Analyte	Ionic Liquid	Electrode	Analyte Concentration	Ref.
	Poly[DADMA][NTf2]			
O_2 and **NH_3**	[C2mim][BF4] and [C4mim][BF4]	Gel polymer electrolyte (ILs in PVDF) between planar electrodes	1–20% for O_2; 1–10 ppm for NH_3	[54]
O_2 and **H_2**	[Bmpy][NTf2]	Planar Pt-Ni alloy electrodes	500–5000 ppm for O_2; 500–6250 ppm for H_2	[55]
H_2				
	[C4mim][NTf2] and [C4mpyrr][NTf2]	Clark-type sensor with polycrystalline Pt gauze	0.05–1.25%	[56]
	[C4mim]Cl	Pd deposited on carbon gas diffusion electrode	1–5%	[57]
	[Bmpy][NTf2]	[Bmpy][NTf2] on Pt/C/Nafion screen-printed electrode	2000–10,000 ppm	[58]
	[C2mim][NTf2]	Au microchannel electrodes with electrodeposited Pt nanoparticles	0.1–10%	[59]
NH_3				
	[C2mim][NTf2]	Pt SPE, TFE, MATFE, and microdisk	10–100 ppm	[60]
	[C2mim][NTf2]	SP electrode, thin-film electrode (TFE), microarray thin-film electrode (MATFE), and microdisk.	10–100 ppm	[61]
	[C2mim][NTf2]	Pt MATFE	10–100 ppm	[62]
	[C2mim][NTf2]	Pt-based MATFE (with different morphologies)	1–2 ppm LODs (depending on the morphology)	[62]
NH_3 and **HCl**	[C2mim][NTf2] and [C4mpyrr][NTf2]	Au microchannel electrodes	20–100 ppm	[63]
VOC (in air)	[C4mpyrr][NTf2]	Clark-type sensor with polycrystalline Pt gauze	200–3000 ppm of acetaldehyde	[64]
CO_2	[Bmpy][NTf2]	Au microchannel electrodes with electrodeposited Cu nanoparticles	0.14–11%	[65]

Analyte	Ionic Liquid	Electrode	Analyte Concentration	Ref.
Hexanaldehyde (HA)	[Bmim][OH]	Pt microelectrodes	2–300 ppm (HA in squalene)	[66]
C_6H_6 and HCHO	[C2mim][EtSO$_4$]	IL and ionogel (IL in poly(N-isopropylacrylamide)) between interdigitated electrodes	10–50 ppm	[67]
SO_2	[C4mpyrr][NTf2]	TFEs and MATFEs	1–10 ppm	[68]
H_2O (humidity)	[Bmim][DCA]	IL incorporated in gels on interdigitated electrodes	30–70% RH	[69]
Ethanol	[Bmim][HSO4]	IL on Au screen-printed electrode	1–10%	[70]
NO_2	[Bmim][NTf2]	Solid polymer electrolyte (PVDF + IL) on screen-printed electrodes	1–10 ppm	[71]
	[Bmim][BF4]	Solid polymer electrolyte (ionic liquid (IL), carbon nanotubes + polyaniline + IL) on SP electrodes	0–700 ppm	[72]
Ethylene (C_2H_4)	[Bmim][NTf2]	Solid polymer electrolyte (PVDF + IL) on SP electrodes	100–500 ppm	[73]

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the three, interesting LOD(NH_3) values between 1 and 2 ppm have been reported by Hussein and coworkers using highly porous 3D-structured ("cauliflower-shaped") Pt electrodes prepared via electrodeposition [62].

Ionic liquids reported in table: [C2mim][PF6]: 1-ethyl-3-methylimidazolium hexafluorophosphate; [C2mim][NTf2]: 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide; [C4mpyr][NTf2]: 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide; [N8,2,2,2][NTf2]: triethyloctylammonium bis(trifluoromethylsulfonyl)imide; [C4mim][Cl]: 1-butyl-3-methylimidazolium chloride; [C4mim][BF4]: 1-butyl-3-methylimidazolium tetrafluoroborate; [C4mim][PF6]: 1-butyl-3-methylimidazolium hexafluorophosphate; [C4mim][NTf2]: 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide; [C5mim][PF6]: 1-pentyl-3-methylimidazolium hexafluorophosphate; [MOmim][PF6]: 1-[8-mercaptooctyl]-3-methylimidazolium hexafluorophosphate; [Bmim][BF4]: 1-Butyl-3-methyl-imidazolium-tetrafluoroborate; [Bmim][NTf2]: 1-Butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide; [Emmim][TFSI]: 1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide; [Bmim][NTf2]: 1-Butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide; Poly[DADMA][NTf2]: poly(diallyldimethylammonium bis(trifluoromethylsulfonyl)imide).

Among the possibilities that have been explored in the various works listed in **Table 2** in order to improve the sensing performance, a major one regards the design of the working electrode (WE). As mentioned previously, it is possible to employ porous WE as the initial element encountered by the flowing gas molecules. Alternatively, it is possible to employ a device design in which the gas molecules first partition into the liquid phase and next diffuse towards the WE. An evident advantage of the first design is to improve (shorten) the response time of the device, as the diffusion of gas molecules is usually slow in IL layers. Examples of devices employing a porous WE in Clark-type cell are Refs. [36][45][56][64]. Sensing electrodes are usually in the form polycrystalline Pt gauze materials, while in some cases, these have been functionalized with Pd nanoparticles in order to enhance the reactivity toward the analyte (e.g., [36][57]).

Designs in which the gas first diffuses into the liquid have the advantage (with respect to the previous one) of allowing closer positioning of the electrodes. This allows producing small cells using miniaturized, low-cost electrode geometries, such as screen-printed electrodes (SPEs) or interdigitated electrodes. In such cases, the use of ILs provides a definite advantage over that of conventional electrolytes, as the virtually null volatility of an IL allows the use of small volumes (e.g., [37][43][61]). Similarly, thin-film electrodes (TFEs), interdigitated electrodes, and microarray thin-film electrodes (MATFEs) have been explored in various applications, with many of the most recent ones listed in **Table 2**.

Another new trend in AGS-based research might be opened by the use of the so-called polyionic liquids, also named as poly(IL)s, which are polyelectrolytes combining the peculiar properties of ILs with the physicochemical robustness/stability of polymers. Poly-ILs have been used in other applications (see Ref. [74] for a review on the subject), but only recently have they been explored as electrolytes of AGS devices in a work by Doblinger and coworkers, who demonstrated the possibility of monitoring the oxidation of NH_3 and the reduction of SO_2 and O_2 using ILs/poly(ILs) membranes on an Au-TFE working electrode [53]. The results suggest that the use of poly(ILs) might be one of the future trends in the exploration of electrochemical gas sensors.

Presently, it is quite established that the use of ionic liquids in AGSs has large potentialities, while room for further increases in the sensitivity of the sensors exists, achievable through suitable combinations of the IL ions, the electrode materials/design, and the kind of electrochemical measurements employed; for a further discussion on this topic and sketches of some perspectives, see Ref. [75].

3. Metal–Organic-Framework-Based Composites in Gas Sensing—Recent Developments

3.1. General Properties of Metal–Organic Frameworks

Metal–organic frameworks (MOFs) are solid porous materials which, according to the terminology officially adopted by IUPAC in 2013, are classified as a subclass of coordination networks which are a subclass of coordination polymers [76]. The MOF network (one-dimensional, two-dimensional, or three-dimensional) arises from the strong coordination bonds between metal nodes (metal ions, metal centers, or metal clusters [77]) and the organic linkers. Usually, transition metal ions, especially those of the first row, lanthanides, and some alkaline earth metals are used as metal nodes because of their variable coordination numbers, geometries, and oxidation states [76][78][79]. Organic molecules containing one or more N-donor or O-donor atoms are mostly used as organic linkers, especially carboxylates (either aliphatic or aromatic containing one or more condensed rings), pyridyl (e.g., pyridine, pyrazine and bipyridyl derivatives), cyano compounds, polyamines, and imidazole derivatives; in addition, oxalic acid, phosphonates, sulfonates, and crown ethers are other possible ligands [76][78].

The main distinctive structural features of MOFs are the high porosity, the large volume of the pores (up to 90% of the crystalline volume or more), the large specific surface area (above 5000 m^2 g^{-1}), and the good thermal stability (250–500 °C) due to the presence of strong bonds (e.g., C–C, C–H, C–O, and M–O) [76][78]. Many of these properties are determined by the mutual interaction between specific metal ions and linkers; as a consequence, MOFs' characteristics can be tuned by judiciously selecting metal nodes and linkers to have the desired pore size, structure, and functionality for specific applications [80]. MOFs' 3D structure displays cavities and inner surfaces, which are occupied by counterions, solvate molecules and/or guest molecules. The guest species can significantly extend the designed applications of MOFs [80].

MOF synthesis is performed mainly in the liquid phase by mixing solutions of the ligand and metal salts under solvothermal/hydrothermal conditions at a high temperature and pressure. Other alternative and consolidated synthetic strategies are based on mechanochemical, electrochemical (for large-scale synthesis), microwave, and sonochemical methods. The most recently proposed methods are: ionothermal synthesis [76][81], the slow evaporation method [76], the diffusion method [76][82], the use of a microfluidic device [81], dry-gel conversion (DGC) [81] and microemulsion [76].

MOFs are versatile materials which are attracting great interest for application in environmental and biomedical areas as catalysts, as absorbers for toxic gases and metal ions, as materials for electrochemical devices, as drug carriers, as bioimaging agents and also therapeutic agents [83][84]. Recently, MOFs have been used also as sacrificial templates for the production of metal oxides or metal oxide–carbon hybrids [85] with promising morphological and textural properties to be exploited in sensing and electrochemical applications [86][87]. MOFs also are emerging as novel sensing materials because of their high surface area which enhances detective sensitivity, their specific structural features (open metal sites, tunable pore sizes, etc.) which promote host–guest interactions and selectivity, and flexible porosity which enables the reversible release and uptake of small target molecules [84][88][89].

Presently, the exploitation of MOFs’ potentiality in gas sensing is affected by some limitations [88][90]: (1) Most pure MOFs are not stable under extreme conditions (high temperature and high humidity levels). (2) The types of gases detectable by MOFs are limited. (3) The inherent electrical conductivity of MOFs is low and this limits their use in the development of electronic sensors. (4) The interaction mechanism between MOFs and the analyte is poorly understood. (5) MOFs are generally produced as powders with a generally low mechanical strength and poor processability. This last limitation is particularly relevant since the sensitivity of gas sensors obtained from powders is low and poses the need for a post-process of MOFs as thin films or membranes.

To ensure the potential use of MOFs in sensing applications, most of these concerns must be addressed and, to this aim, the development of new MOF–based materials which have better properties (including processability in harsh conditions) than pure MOFs is gaining a lot of attention [90][91]. Research efforts have been focused on different strategies, including: (i) post-synthetic modifications [92]; (ii) linker change or functionalization; (iii) ion exchange; (iv) active groups grafting; (v) impregnation with suitable active materials; (vi) production of MOF-based hybrids/composites [79][91][92][93].

Among the different possibilities, the common adapted solutions are post-synthetic modifications and the production of hybrids/composites integrating MOFs and functional materials. Post-synthetic modifications involve the introduction of desired functional groups into the MOFs after their synthesis [79][92]. The modification can involve: the heterogeneous exchange of ligands or metal ions by breaking and forming chemical bonds within the original MOF, solvent-assisted ligand exchange, and replacement of the nonbridging ligands and metal nodes [76][92][94]. Mixed-metal MOFs, containing at least two metal ions in their framework, can be prepared under post-synthetic methods and possess new properties and activities due to the presence of the second metal ion. This approach is frequently used to produce MOF-based materials exhibiting improved fluorescent/luminescent properties [92][94].

By combining MOFs with suitable materials, the functionality and the textural/thermal/magnetic/electric properties can be improved to meet specific requirements. In some cases, the hybrid/composite materials exhibit new properties that are superior to those of the individual components since they combine the advantages of both parent materials. Metal oxides [95], polymers [96], metal nanoparticles [97], silica [98], carbon nanotubes [99], graphene-related materials (GRMs) [93][100][101] and quantum dots [102] have been used for the production of MOF-based hybrids and composites [90][91].

A wide variety of methods have been applied for the preparation of MOF composites. The in situ growth approach involves the growth of MOF crystals under solvothermal/hydrothermal conditions in the presence of another functional material [91]. In this type of synthesis, the MOF structure is built from the precursors around and eventually inside the other composite component. This method has been mainly used for the preparation of MOF composites with carbon-based materials [93], metal oxides [103] or with metal nanoparticles [97][103]. During the synthesis, the second material can act also as a templating agent, leading to oriented growth of MOF crystals, and graphene is one such example [104]. In the encapsulation method, the MOF composite is formed starting from the second component precursors and the preformed MOF; namely, the second component forms inside the cages of the MOF and at the end of the synthesis, the particles stay stable inside the cages without directly bonding to the MOF structure [91]. This is the method primarily used for the production of MOF/polymer and MOF/NPs composites [91][96]. Solid grinding and impregnation are other strategies to incorporate NPs in MOFs [105][106]. The electrospinning and solution-blending methods are two possible approaches for the preparation of MOF/polymer membranes [103]. MOF composites for biomedical applications have been also produced by coating the MOF structure with silica or a specific polymer with the aim of reducing their cytotoxicity and intrinsic instability under physiological conditions [103].

The huge and wide variability in pore size distribution of MOFs allows different guest molecules with different characteristics (size, acid–base behavior, polarization, etc.) to easily access the cavity and interact with the pore surface due to the presence of unsaturated metal sites and Lewis acidic/basic sites [89][107]. In such a way, specific MOF properties can be influenced, and changes in optical, electrical, and mechanical MOF properties can occur [88][108]. On this basis, various MOFs have been developed for possible use as chemiresistive, magnetic, ferroelectric, colorimetric, as well as luminescent sensors [88][109][110]; many examples are reviewed in this section. The high porosity of MOFs and the easy reversibility of the interaction with the target guest molecule are valid prerequisites to achieve repeatability, regeneration and robust operability under repeated detection cycles. On the other side, signal transduction is a major challenge for the efficient utilization of MOFs in chemical sensing [89].

The sensitivity of MOF-based detection largely depends on the sensing method used for signal transduction. MOFs are generally coupled with such several signal transduction techniques and tools as chemiresistors, interferometry, quartz crystal microbalance (QCM), surface acoustic wave (SAW), and microcantilevers (MCLs). MOF-based thin-film techniques have hence been very recently suggested as a valid advantage for developing next-generation chemical sensors [110]. Moreover, recently, conductive MOFs have been synthesized by using proper organic ligands or doping with conductive materials to form hybrids and composites with the aim of generating detectable changes in resistance/capacitance upon guest-molecule exposure [111].

An overview of several different sensing mechanisms involving MOFs and the mainly detected gas types is provided in **Figure 1** and detailed in the following sections.

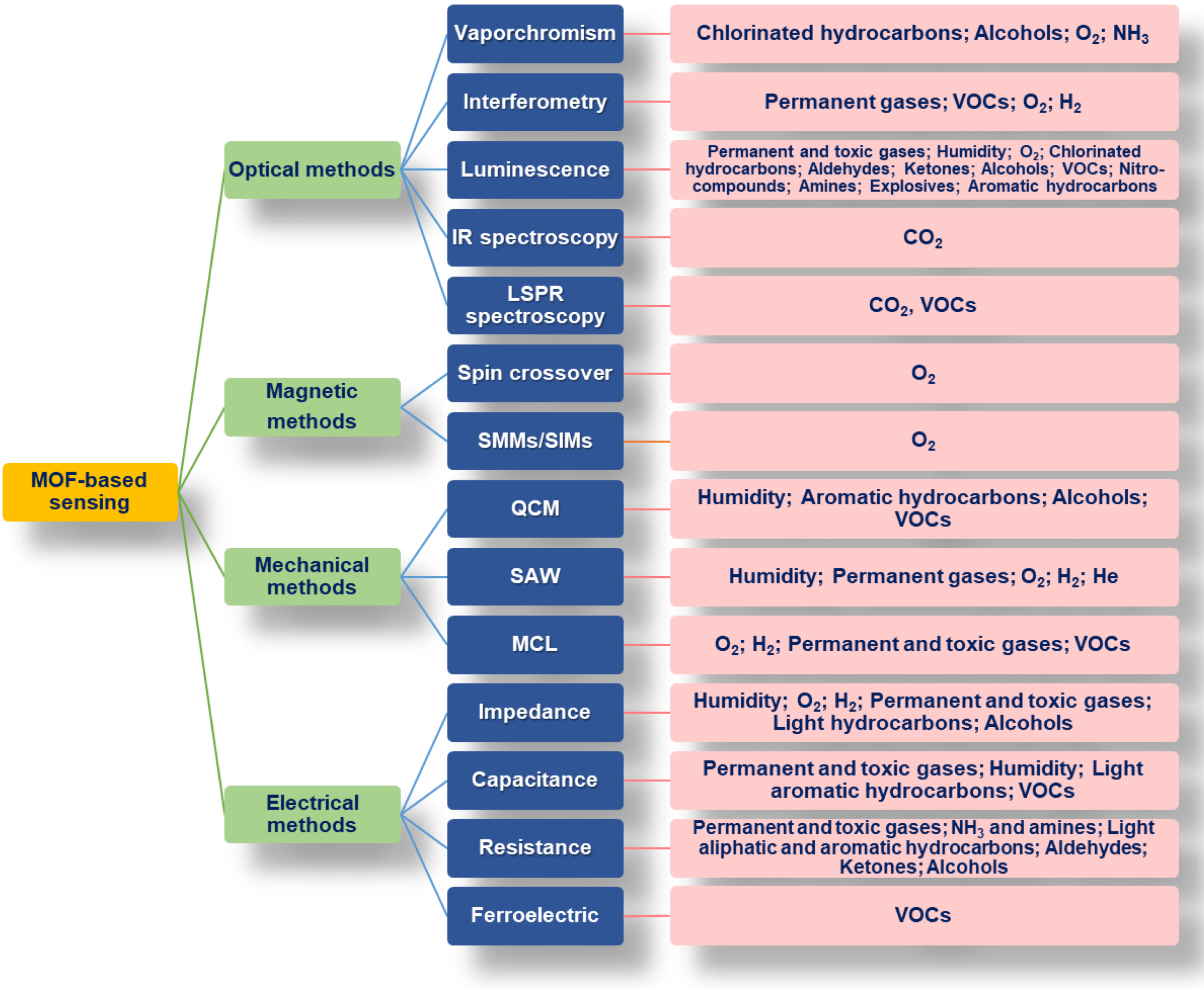

Figure 1. Scheme of the various methods employing MOF materials for chemical sensing.

3.2. MOF-Based Sensors Using Gravimetric and Mechanical Methods

The easier approach for gas detection utilizing MOFs is the measurement of changes in MOF mass as the material selectively adsorbs the target analyte. This can be performed on a macroscale, bulk scale, or by using thin films deposited on a mechanical resonator. In this last case, the change in mass of the resonator due to gas adsorption is translated into an electrical signal [107].

In these mechanical methods, at first, an analyte is adsorbed into the pores of MOFs grown on electromechanical devices and then the mass changes are converted into an electrical signal through different transduction mechanisms (shifts in frequency or changes in the work function) [107]. In this framework, an important aspect is related to the characteristics of the MOF films: a tight contact between the MOF film and the electromechanical-device surface is strictly required to obtain the suitable sensitivity.

The main gravimetric and mechanical methods involving MOFs for gas-sensing applications are based on the following electromechanical devices:

3.2.1. Quartz Crystal Microbalance (QCM)-Based Sensors

In QCM-based sensing, a thin piezoelectric quartz crystal is the core component of a QCM transducer [112]. After being electroplated, the thin slice oscillates when an alternating current (AC) is applied. The mass increases upon the adsorption of analyzed gas molecules, and the resonant frequency decreases (**Figure 2**) [112].

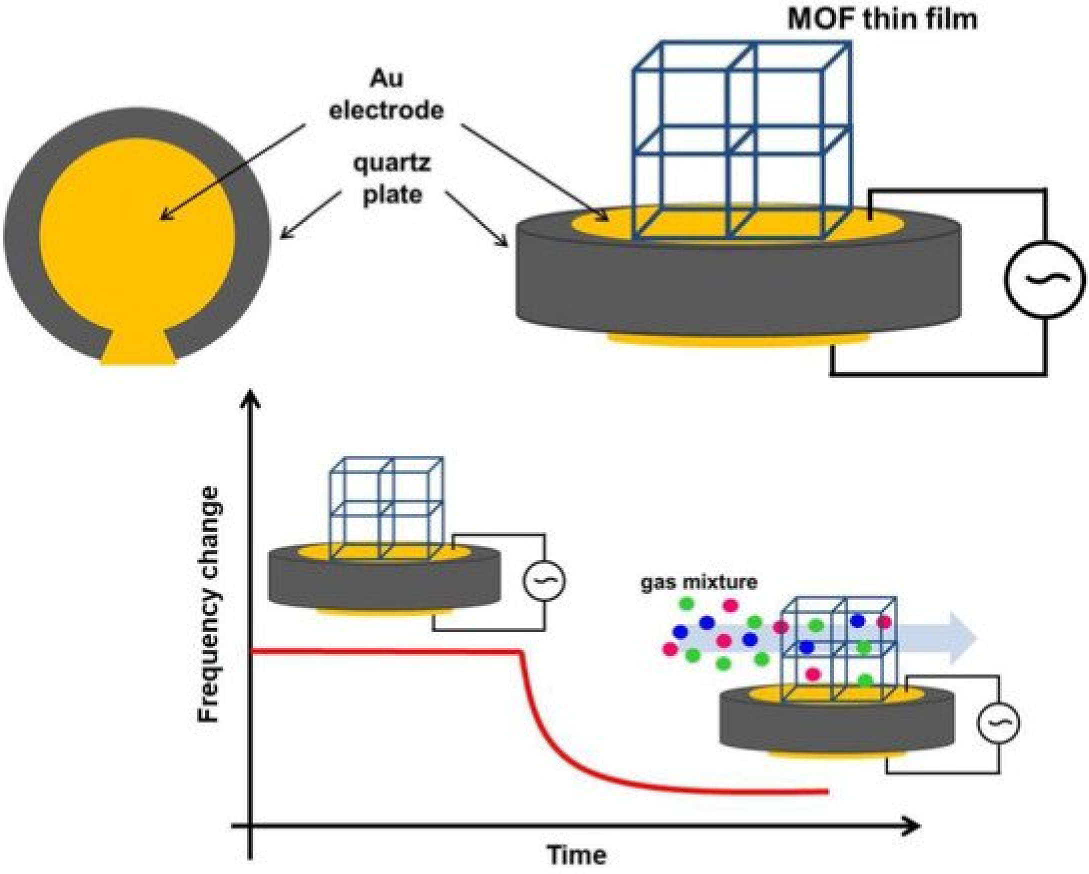

Figure 2. Scheme of MOF-based QCM gas sensor.

QCM-based MOF gas sensors have been successful in sensing a wide range of analytes using both reversible and irreversible interactions [108][113], even if little chemical identity or selectivity information can be directly obtained. QCM-based MOF sensors have been mainly proposed for humidity, VOC and hydrocarbon detection [108][113]. For example, Ma et al. used a MOF-based QCM gas sensor to detect inert and nonpolar gases such as BTEX (benzene, toluene, ethylbenzene, and xylene) [114]. To address the cross-sensitivity issue, QCM sensor arrays based on the combination of different MOFs to detect the same gas mixture have been recently proposed. Such a cross-sensitive sensor can be defined as an electronic nose (e-nose) [89].

3.3.2. Surface Acoustic Wave Sensors (SAWS)

In surface acoustic wave sensors (SAWS), the gas adsorption is detected by measuring the frequency shift of acoustic waves generated by a quartz oscillator vibrating and traveling parallel to the surface [115]. The response of this device is reproducible and faster as compared to the same coating on QCMs, but it is dependent on the film thickness: for each device, an optimal thickness can be estimated, above which the sensor response saturates [89]. Examples of MOF-based SAWS have been proposed by Paschke et al. (MOF@SAW sensor based on MFU-4 for the detection of H_2, N_2, CO_2) [116], Devkota et al. (ZIF-8-coated SAW reflective-delay-line mass sensors for the sensitive detection of CO_2 and CH_4 at ambient conditions) [117] and by Vanotti et al. (SAW device functionalized with ZnTACN for CO_2 detection) [118].

3.2.3. Microcantilever-Based Sensors (MCLs)

Gas detection by microcantilever (MCLs) sensors are characterized by two transduction mechanisms: the changes in the cantilever oscillation frequency caused by mass uptake and the strain-induced bending [119]. In the former mode, changes in the sensor oscillation frequency are typically detected optically. In the latter mode, adsorption produces strain at the coating’s MCL interface, causing deflection of the cantilever beam that can be detected either optically or by using a built-in piezoresistive sensor. The structural flexibility of MOFs is an advantage for chemical detection using static MCL, because even small changes in the unit cell dimensions can result in large tensile or compressive stresses at the interface between the cantilever and the MOF thin film [120]. However, MCL-based sensors are scarce in practical applications, due to cross-sensitivity and poor selectivity; indeed, in the case of exposure to a gas mixture with multiple components, all constituents can be absorbed. Different kinds of MOFs have been proposed for the development of MCL-based gas sensors: UiO-66 for toxic organophosphorus molecules [121]; MIL-53 (Al) for CO_2, N_2, CO, and Ar [122]; and HKUST-1 for the detection of VOCs [123].

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