Highly selective gas sensing enabled by filters

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Portable and inexpensive gas sensors are essential for the next generation of non-invasive medical diagnostics, smart air quality monitoring & control, human search & rescue and food quality assessment to name a few of their immediate applications. Therein, analyte selectivity in complex gas mixtures like breath or indoor air remains the major challenge. Filters are an effective and versatile, though often unrecognized, route to overcome selectivity issues by exploiting additional properties of target analytes (e.g., molecular size and surface affinity) besides reactivity with the sensing material. This review provides a tutorial for the material engineering of sorption, size-selective and catalytic filters. Of specific interest are high surface area sorbents (e.g., activated carbon, silica gels and porous polymers) with tunable properties, microporous materials (e.g., zeolites and metal–organic frameworks) and heterogeneous catalysts, respectively. Emphasis is placed on material design for targeted gas separation, portable device integration and performance. Finally, research frontiers and opportunities for low-cost gas sensing systems in emerging applications are highlighted.

1. Introduction

Gas sensors allow modern electronic devices to smell their environment. By utilizing portable and inexpensive sensors, a multitude of promising applications can be realized (Fig. 1):

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diseases (e.g., cancer or diabetes) and monitor their progression, or personalized tracking of physiological data (e.g., dieting or exercise); and in human search and rescue to assist first responders with robots capable to detect the unique human chemical signature similar to dogs (e.g., after earthquakes or avalanches), just to highlight some.

For integration into electronic devices, gas sensors need to be compact, inexpensive and simple-in-use. Most importantly, they need to detect selectively volatile organic compounds (VOCs) and gases at low ppb to ppm (parts-per-billion/million by volume) concentrations in mixtures without interference over hundreds of others (e.g., > 800 in breath or > 250 in indoor air). State-of-the-art gas sensors (e.g., chemoresistive or optical) provide this sensitivity by making use of nanomaterials having high specific surface area (e.g., 5 ppb acetone at 90% relative humidity (RH) by leached nanostructured Pd/SnO$_2$ or sub-ppb detection of Cl$_2$ by nanoparticle-based liquid crystal sensors).

Most challenging, however, is selectivity, which can be tuned to some extent by material composition of single sensors including metastable phases, solid solutions, mixed oxides or heterostructures with unique morphology (e.g., hollow nanofibers or ordered macroporous oxides). For example, the epsilon phase of WO$_3$ (i.e., ε-WO$_3$) stabilized by Cr-doping showed some acetone selectivity (> 6) to ethanol, methanol, NO$_x$, NH$_3$ and CO. Also, In$_x$Sn$_{1-x}$O$_{1.2}$ reacts selectively to formaldehyde, Ti/ZnO to isoprene, Si/α-MoO$_3$ to ammonia, or Ag/LaFeO$_3$ to methanol. However, such selectivities are typically only moderate, apart rare exceptions exploiting unique analyte-sensor interactions (e.g., CuBr for ammonia or WO$_3$ for NO$_2$). This is often not sufficient in applications where interfering concentrations may be orders of magnitude higher than the target analyte (e.g., < 8 ppb carcinogenic formaldehyde in indoor air with ~1000 ppb CO background).

To discriminate between analytes in gas mixtures, different sensors can also be combined to arrays (also called electronic

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**Fig. 1** Compact and low-cost gas sensors in air quality monitoring, agriculture & food quality assessment and health & lifestyle applications.

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noses or E-noses), overcoming selectivity limitations of single sensors.38 Reviews on material design,39 data processing algorithms40 and applications (e.g., food quality and safety monitoring,41 or breath analysis42) of sensor arrays address their potential. Generally, arrays process different sensor signals by statistical models to classify different odors. A variety of algorithms is used based on descriptive43 (e.g., principle component analysis, hierarchical cluster analysis) and predictive methods44 (e.g., artificial neural networks), often requiring a large set of data to “train” the models. Typically, arrays do not detect and discriminate specific analytes, but rather distinguish and classify analyte patterns (i.e., odors). For instance, a sensor array might differentiate lung cancer patients from healthy subjects45 or distinguish different quality grades of Indian black tea.46 Thereby, often broadly sensitive sensors are used, making the array susceptible to overfitting and bogus correlations from confounders.47 To discriminate multiple analytes and detect them with high accuracy in gas mixtures, distinctly selective sensors, ideally with orthogonal features,48 are most desirable for inclusion into arrays.

Filters represent a third approach to enhance the selectivity of gas sensors. They were first discussed in a review about selectivity in semiconductor gas sensors in 1987.49 Since then, filters were treated only as a side aspect in many books and reviews of gas sensors in general,50 gas sensor types (e.g., metal-oxide,51 arrays,52 zeolite,53 metal–organic frameworks,54 mesoporous materials,55 combustible56) and applications (e.g., environment, health and safety,57 automotive,58 explosives,59 pollution,60 indoor air quality,2 health monitoring and disease diagnostic61). Placed either in front (e.g., packed beds) or directly on top (e.g., overlayers) of sensors, filters alter the composition and/or concentration of analytes in gas mixtures before reaching the sensor. In the ideal case, the target analyte is not affected while interferants are removed, resulting in high selectivity (>1000) even with non-selective sensors.52 Already in 1980, a packed bed of zeolite 3A was tested to filter H2S to selectively detect H2 by a commercial SnO2 sensor (Taguchi, Figaro).52 Also, SiO2-covered SnO2 sensors eliminated interference by CO, CH4, ethanol and isobutane for selective H2 detection,63 charcoal and carbon cloth were used to protect CH4 sensors from poisoning by siloxanes,64 and zeolite 5A filters blocked H2S and ethylene for selective CO detection.65 Today, filters are well-established in most industrial sensors (e.g., CO66 and CH467 alarm sensors), however, their immense potential remains rather unexplored.

Only recently, filters were used to overcome selectivity issues of sensors for other, so far inaccessible, applications such as revealing methanol-adulterated liquors by separating methanol from ethanol in a packed bed sorption filter,68 detecting H2 leaks to fulfill, for the first time, stringent national standards by a polymer membrane on top of a plasmonic sensor,69 and monitoring body fat burn from breath acetone by combusting interferants on a Pt/Al2O3 filter70 preceding a Si/WO3 sensor. Thereby, the distinct advantage of filters is the exploitation of additional and complementary molecular properties (e.g., size, sorption affinity), often not accessible by sensors alone. By using advanced materials (e.g., microporous metal–organic frameworks, MOF) and material design on the nanoscale (e.g., heterostructures, nanocluster dopants), filters can be designed systematically to achieve high sensor selectivity. Most importantly, filters can be modular to the sensor and thus flexibly combined with different sensor technologies (e.g., optical,69 chemoresistive,71 electrochemical72) and even sensor arrays.73

Here, we systematically review sorption, size-selective and catalytic filters with guidelines for their design in assembling highly selective sensor systems. Selectivity improvement by filters comes at increased complexity of the sensing system and each filter type introduces distinct advantages and disadvantages, broadly summarized in Table 1. We address these characteristics by first introducing the underlying filter concepts and basic principles necessary for analyte separation. Then, specific implementations of such filters are presented, highlighting trends and critically comparing their performance. Finally, device integration and performance in practical cases are elaborated. We close by highlighting current challenges and opportunities.

### 2. Sorption filters

#### Definitions & principles

A sorption filter exploits the difference between analytes flowing or diffusing through. So mixtures of analytes either adsorb74 onto or are absorbed in the filter to enhance the sensor selectivity downstream. Most sorption filters are based on adsorption, while absorption dominates gas chromatography (GC)-sensor systems.

#### Table 1 Performance characteristic of different filter types (○, ↑, ↓ indicating no change, increase and decrease in comparison to the sensor without filter, respectively)

| Filter type  | Configuration         | Selectivity | Flexibility for selectivity | Multi-analyte detection | Sensitivity | Analysis time | Power consumption | Size |
|--------------|-----------------------|-------------|-----------------------------|-------------------------|-------------|--------------|-------------------|------|
| Sorption     | Packed bed            | ↑           | ↑                           | ○                       | ○           | ○            |                   | ↑    |
|              | Separation column     | ↑           | ↑                           | ↑                       | ↓           | ↑            | ↑                 | ↑    |
| Size-selective| Overlayer            | ↑           | ↑                           | ○                       | ○           | ○            |                   | ○    |
|              | Membrane              | ↑           | ↑                           | ↓                       | ↑           | ↑            |                   | ↑    |
| Catalytic    | Overlayer             | ↑           | ↑                           | ○                       | ↑           | ○            |                   | ○    |
|              | Packed bed            | ↑           | ↑                           | ○                       | ○           | ○            |                   | ↑    |
These filters are inexpensive and modular to the gas sensor, thus easy to implement and characterize. Most importantly, they are flexible as a wide range of sorbents is available to separate analytes based on polarity, hydrophilicity, boiling point, molecular weight or size. A drawback is their saturation, requiring replacement or regeneration by purging with clean air and/or by heating that tends to prolong sensor response and recovery times. However, by combining purging and heating, adsorbents can be regenerated within minutes as established for thermal desorption tubes in air quality monitoring.81

For adsorption, the chemical surface groups (nonpolar, polar and analyte-specific), accessible surface area and pore size distribution of the adsorbent (filter) are important (Fig. 2a). Adsorption of analytes takes place through weak (10–100 meV) and reversible physical forces (i.e., van der Waals).82 Sorption filters are often packed beds of adsorbent particles, porous granules or fibers. To characterize their adsorption capacity for certain analytes, a breakthrough curve is recorded.83 Thereby, the analyte concentration at the filter outlet is measured for constant inlet analyte concentration and flow rate. The time for the outlet analyte concentration to reach a certain fraction (often 5%) of its inlet is defined as the breakthrough time.

Decreasing the flow rate through the filter (adsorbent) prolongs the breakthrough time linearly (Fig. 2b), but typically lowers the sensor response as fewer analyte molecules reach the sensor.85 Breakthrough time multiplied by the flow rate gives the breakthrough volume that is flow-rate-dependent and increases proportionally with adsorbent loading since more surface area is available for analyte adsorption (Fig. 2c).85 However, larger filter loadings result in larger pressure drop through the filter and prolong the sensor response time. Typically, the breakthrough volume is normalized with respect to adsorbent loading.89 This material-specific property is useful in design of sorption filters and independent (for a wide range) of flow rate and adsorbent loading. At low analyte concentrations (<10 ppm), breakthrough volumes are independent of concentration, as typically seen in GC.90 This is important for gas sensing in breath analysis or indoor air monitoring where analyte concentrations are in that range (e.g., ~500 ppb acetone in breath91 or ~80 ppb formaldehyde in indoor air92). But concentrations can reach also hundreds of ppm in certain conditions (e.g., ethanol from cleaning products93 or propane/butane from gas cookers), where breakthrough occurs earlier as the capacity of adsorbent is exhausted. This is shown exemplarily in Fig. 2c for adsorption of 85–539 ppm hexane on a porous non-polar polymer adsorbent with large surface area (Chromosorb 106, >700 m² g⁻¹).85

Adsorption by physical forces is temperature-dependent (van’t Hoff law) resulting in a steep decrease of breakthrough volumes with increasing temperature. This is shown in Fig. 2d for adsorption of hexane on a porous non-polar polymer adsorbent (Tenax TA), where increasing the temperature from 0 to 20 °C reduces the breakthrough volume by 95%.80 Heating is used to accelerate regeneration of sorption filters (e.g., packed zeolite bed73 for CH₄ sensing within 2 h by heating to 250 °C) and control the separation of compounds by GC.95 Another factor is relative humidity (RH) that is omnipresent in most applications (e.g., up to 95% at 36 °C in exhaled human breath96). Adsorption of water leads to partial blocking of adsorption sites and reduces the breakthrough time, depending on adsorbent hydrophilicity. For instance, increasing the RH from 0 to 61% for weakly polar activated carbon fibers reduced the breakthrough time of benzene by 76% (Fig. 2e). In contrast, when using the non-polar polymer adsorbent Tenax TA, this time was not affected.97

Adsorbent materials & properties

Sorption filters preceding gas sensors are tabulated in Table 2, showing their composition, target analytes and figures of merit. First sorption filters for gas sensing were carbon-based (i.e., activated carbon, graphene, carbon molecular sieve, carbon fiber, etc.) as these were well established already for vapor filtration (e.g., gas masks98). Other important adsorbents include silica (silica gel99 and mesoporous silica100), porous polymers (e.g., Tenax TA101), activated alumina,102 zeolites103 and metal–organic frameworks (MOFs).104 These feature high

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The image contains a figure (Fig. 2) labeled as follows:

- **a**: Critical adsorbent (filter) properties: surface chemical groups, surface area and pore size distribution.
- **b**: Effect of overall flow rate through the filter on the breakthrough time.84
- **c**: Effect of filter (adsorbent) loading and analyte concentration on breakthrough volume.85
- **d**: Effect of temperature on specific breakthrough volume.80
- **e**: Effect of RH on the breakthrough time.86
porosity and surface area (Fig. 3a–d), resulting in high adsorption capacity. They are commercially available in a variety of shapes (e.g., powders, granules, pellets, fibers), specific surface areas, pore sizes and chemical functionalization (e.g., surface polarity). Specific surface areas range usually from 20 m$^2$ g$^{-1}$ for some porous polymers (e.g., Tenax GR) up to 7000 m$^2$ g$^{-1}$ for ultra-high surface area MOFs (Fig. 3e).

Carbon-based adsorbents, silica gels, porous polymers and activated alumina typically feature a mix of meso- (2–50 nm) and micropores (<2 nm) with similar log-normal pore size distributions. Zeolites and MOFs on the other hand, have a well-defined micropore size in the same order of magnitude as gas molecules (e.g., kinetic diameter of benzene is 0.59 nm) that depends on their composition. The accessible surface area, and thus adsorption capacity, depends often on adsorbent’s pore size and analyte’s molecular size. For instance, $p$-xylene can access the pores of adsorbent MOF-107, while $m$- and $o$-xylene cannot, resulting in enhanced adsorption capacity.

### Table 2  Sorption filters in combination with gas sensors

| Filter configuration | Filter material | Target analyte | Sensor | LOD* (ppm) | Response time | Tested interferants (selectivity) | Ref. |
|----------------------|----------------|---------------|--------|------------|--------------|----------------------------------|------|
| Packed bed           | Activated carbon | CH$_4$ | Pellistor | 25 000 | — | Hexamethyldisiloxane (x$^b$) | 59 |
|                      | Ag/Al$_2$O$_3$  | Ethylene     | SnO$_2$ | 20       | 2.5 min     | Ethanol (0.11), H$_2$ (0.07) | 76 |
|                      | Carbon cloth   | CO           | SnO$_2$ | 15       | —           | Acetylene, NO, NO$_2$, SO$_2$ (all x$^b$) | 141 |
|                      | Carbon cloth, charcoal granules | CH$_4$ | Pellistor | 10 000 | 12–50 s | Ethane, ethanol, ethyl acetate (all x$^b$) | 66 |
| Indigo               | Ozone          | Electrochemical | SnO$_2$ | 0.04 | ~5 min      | NO$_2$ (x$^b$) | 143 |
| Indigo/carbon nanotubes | NO$_2$ | Organic semiconductor | SnO$_2$ | 0.01 | — | Ozone (x$^b$) | 145 |
| Zeolite 4A           | H$_2$          | Electrochemical | SnO$_2$ | 10 | 5 s | H$_2$S (x$^b$) | 62 |
| Zeolite 5A           | CO             | Electrochemical | SnO$_2$ | 0.03 | 5 s | Ethylene (x$^b$), H$_2$S (x$^b$), CH$_4$ (>1000), ethane (>1000), H$_2$ (>1000) in liquid | 65 |
| Zeolite MOR          | CH$_4$         | SnO$_2$ | 1000 | — | — | Ethanol, hexane (both x$^b$) | 75 |
| Commercial GC column | Hayesep Q      | H$_2$, CH$_4$ | SnO$_2$ | 2 | <1 min | — | 158 |
| MXT-1                | VOCs (<14 carbon atoms) | PID$^a$ | <0.015 | 30 min | — | — | 161 |
| OV-1 megabore        | Alcohols, acetaldehyde, acetone, ethyl acetate | In$_2$O$_3$ | 0.1 | <5 min | — | — | 159 |
| OV-101               | Alkanes        | TCD$^d$      | — | 5 s | — | — | 154 |
| Rtx-VMS              | cis-1,2-Dichloroethylene, benzene, trichloro-ethylene, toluene, terachloroethylene, $p$-xylene | PID | $1 \ \mu$g L$^{-1}$ | 15 min | — | — | 157 |
| Rtx-5                | 8 organophosphates/sulfates, 5 VOCs | NEMS$^e$ | 0.1 | 5 s | — | — | 158 |
| Rtx-VMS, Rtx-200     | Benzene, ethylbenzene, toluene, xylenes | PID | 0.0025 | 19 min | — | — | 160 |
| Rtx-5MS, Rtx Q-BOND  | 50 VOCs        | PID | — | 14 min | — | — | 162 |
| Not specified        | Acetone        | ZnO           | 0.1 | 2 min | — | — | 156 |
| Separation column    | Activated alumina | Isoprene | Pt/SnO$_2$ | 0.005 | 4 s | Acetone, ethanol, methanol, NH$_3$ (all x$^b$) | 71 |
| Tenax TA             | Methanol       | Pd/SnO$_2$ | 1 | 102 s | — | Acetone, ethanol, H$_2$ (both x$^b$) | 68 |
|                      | Ethanol, methanol | Pd/SnO$_2$ | 0.01 vol% | 10 min | — | — | 175 |
|                      | Formaldehyde   | Pd/SnO$_2$ | 0.005 | 2 min | — | Acetaldehyde, acetone, CH$_4$, CO, ethanol, methanol (all x$^b$) | 176 |
| Overlayer            | Indigo         | NO$_2$ | Organic semiconductor | 0.04 | >1 h | Ozone (>20) | 144 |

*a* Lowest measured concentration. $^b$ Not detectable by the sensor. $^c$ Photoionization detector. $^d$ Thermal conductivity detector. $^e$ Nanoelectromechanical system.
adsorption capacity of \( p \)-xylene.\(^{110}\) When applied as dense layers or membranes, such an effect can even be used to create a sharp size cut-off (e.g., dehydration of solvents by zeolite membranes\(^{111}\)). Also the adsorbent surface properties are crucial and can be controlled thermally (e.g., higher surface area of activated carbon at higher pyrolysis temperature\(^{112}\)) and chemically\(^{113}\) (e.g., alkali treatment of activated carbon to increase adsorption of hydrophobic VOCs,\(^{114}\) plasma/microwave treatment,\(^{115}\) ammoniation\(^{116}\) or oxidation\(^{117}\)).

Sorption filters of relatively non-polar carbon-based adsorbents (e.g., charcoal, activated carbon) are used to remove VOCs that interfere with the selective detection of relatively inert, non-polar gases such as \( \text{H}_2 \), \( \text{CO} \) or \( \text{CH}_4 \) (Fig. 4a). On non-polar adsorbents, VOCs are adsorbed mostly by non-specific dispersion forces that are proportional to VOC’s molecular weight.\(^{121}\) Such filters have been used in commercial CO sensors to meet national standards.\(^{76}\) For instance, the ethanol response of a \( \text{SnO}_2 \) sensor is reduced by more than an order of magnitude with a charcoal filter (Fig. 4b, open vs. filled squares), in contrast to CO (circles) and \( \text{H}_2 \) (triangles) that are not affected.\(^{76}\) Also other VOCs, such as butane, heptane, ethyl acetate\(^{66}\) and silicones\(^{59}\) are filtered out, resulting in highly selective detection of small, non-polar gases (e.g., \( \text{CH}_4 \)).\(^{76}\)

In contrast, polar adsorbents interact with analytes mostly through dipole–dipole\(^{122}\) and hydrogen bonding,\(^{123}\) resulting in more specific molecule removal (e.g., alcohols, carbonyls, aldehydes). Such polar adsorbents, including activated alumina,\(^{124}\) silica gel,\(^{125}\) \( \text{P}_2\text{O}_5 \),\(^{126}\) \( \text{NaF} \),\(^{127}\) metal–organic pastes,\(^{128}\) \( \text{CaCl}_2 \)\(^{129}\) and \( \text{NaOH} \),\(^{130}\) also strongly adsorb water. So, they are used as desiccants to minimize the impact of...
humidity that compromises sensor performance (e.g., SnO₂).\textsuperscript{131} For example, activated alumina is covered by a thin water layer in the presence of humidity\textsuperscript{132} that adsorbs hydrophilic analytes such as alcohols, ketones and ammonia by hydrogen bonding, while hydrophobic hydrocarbons are not affected (Fig. 4c). This facilitated selective sensing of isoprene, a non-invasive marker for cholesterol and other metabolic conditions,\textsuperscript{133} by a packed bed filter of commercial activated alumina (1 g only) upstream of a non-selective Pd/SnO₂ sensor at 90% RH.\textsuperscript{1} While that sensor without filter is not selective (Fig. 4d), only isoprene is detected with the filter during 40 s of exposure before hydrophilic analytes break through (e.g., acetone after 52 s). This is much shorter than typically obtained with carbon-based filters (\(> 1 \text{h}\)) due to their much higher surface area (\(> 1000 \text{ vs. 155 m}^2 \text{ g}^{-1}\), for activated carbon and alumina, respectively), but sufficient for end-tidal breath measurements\textsuperscript{135} and buffered samplers.\textsuperscript{136} The resulting isoprene selectivity by using this filter outperforms\textsuperscript{71} other TiO₂,\textsuperscript{137} Ti/ZnO\textsuperscript{38} and h-WO₃\textsuperscript{139} sensors for isoprene.

More specific interaction includes silver ions that adsorb ethylene quite selectively due to \(\pi-\pi\) interactions.\textsuperscript{140} This was used for selective detection of ethylene for monitoring fruit ripeness using an Ag-doped alumina filter.\textsuperscript{141} After sampling and trapping of ethylene, it is released by heating the filter to 60 °C, and detected by a non-specific amperometric sensor without interference by NO, NO₂, SO₂ and acetylene.\textsuperscript{141} Another example is indigo, whose reactive C=C bond selectively reacts with ozone.\textsuperscript{142} This is used by NO₂ sensors in the form of indigo-impregnated filter paper,\textsuperscript{143} indigo layers directly deposited on a semiconducting sensor\textsuperscript{144} or indigo dispersed in a packed bed of carbon nanotubes\textsuperscript{145} to mitigate interference by ozone. Using differential sensing techniques, such indigo filters were even used for selective ozone detection.\textsuperscript{143} Such analyte-specific interactions were obtained also during formation of chemical complexes,\textsuperscript{146} for instance, ammonia with CaCl\textsubscript{2},\textsuperscript{147} or CuBr\textsubscript{2} forming Cu(NH₃)₂⁺. The first was used to reduce ammonia concentrations in breath from 10 ppm to only 0.8 ppm while other breath analytes were not influenced.\textsuperscript{129} The second has been applied for sensing ammonia down to 5 ppb at room temperature and 90% RH,\textsuperscript{148} but could be used as filter as well. Also quite promising for sorption filters is chemical derivatization, used for instance for selective removal of aldehydes in gas mixtures (e.g., indoor air) by 2,4-dinitrophenylhydrazine.\textsuperscript{4} Another option is surface acidity/basicity tuning for preferential adsorption of bases/acids (e.g., acetic acid on basic Y/ZnO\textsuperscript{149}).

Analyte separation in time

Sorption filters can also act as GC columns to separate analytes in time rather than remove them completely.\textsuperscript{150} For this, the analyte-containing gas sample is carried through the filter by a gas (e.g., helium, nitrogen and rarely air) with a pump or pressurized gas cylinder. Most GC-sensor systems (partition or gas–liquid GC)\textsuperscript{155} use open tubular columns (coated with a liquid phase on the inside),\textsuperscript{150} which are heated to control analyte separation.\textsuperscript{151} If the elution (retention) times of analytes are quite apart, analytes can be detected sequentially by the sensor resulting in very high selectivity and multi-analyte detection capacity (e.g., H₂ and CH₄ in breath\textsuperscript{152}). An inherent drawback of GC-sensors is their batch nature, preventing continuous monitoring of analytes. However, by miniaturizing GC-systems for low sample and dead volumes and optimizing column heating protocols, analysis time can be reduced to a few seconds.\textsuperscript{153}

The first GC-sensor systems were combinations of GC columns with a portable gas sensor.\textsuperscript{154} They selectively detected a variety of analytes, including formaldehyde,\textsuperscript{155} breath acetone,\textsuperscript{156} VOCs from groundwater headspace,\textsuperscript{157} H₂ and CH₄,\textsuperscript{158} alcohols\textsuperscript{159} and aromatics\textsuperscript{160} with limits of detection as low as 15 ppt.\textsuperscript{161} Even highly complex mixtures of up to 50 analytes\textsuperscript{162} could be separated by 2-dimensional GC techniques (two columns in series) with validated performance for occupational exposure monitoring.\textsuperscript{163} Such GC-sensor systems are available commercially, for instance the Defiant TOCAM\textsuperscript{164} or Dräger X-pid\textsuperscript{165} for broad chemical analysis or the Quintron Breath Tracker\textsuperscript{152} for breath H₂ and CH₄ in the diagnosis of lactose malabsorption. However, such systems are expensive (several hundred dollars for the column alone), bulky (coiled column of several meters length), heavy (several kg) and require high power (for heating of the column), making them not suitable for battery-powered and handheld detectors.

Micro GC-sensor systems can be based entirely on micro-electromechanical systems (MEMS)\textsuperscript{166} using planar (i.e., microchip) GC columns,\textsuperscript{154} resulting in much smaller and portable systems, i.e., mountable on a belt\textsuperscript{167} (Fig. 5a). Such systems can reach separation performance close to benchtop GCs, as illustrated in Fig. 5b where 21 different VOCs are separated within 200 s by a GC-flame ionization detector (FID, red chromatogram) and the micro GC-sensor system (blue chromatogram).\textsuperscript{167} They have been tested with a variety of analyte mixtures, including indoor air pollutants,\textsuperscript{168} lung cancer biomarkers,\textsuperscript{169} chemical warfare agents,\textsuperscript{170} aromatics,\textsuperscript{171} trichloroethylene in indoor air,\textsuperscript{172} explosive markers\textsuperscript{172} or VOCs for workplace exposure safety.\textsuperscript{174} However, GC-sensor devices with proven performance under real conditions validated with a benchtop device (e.g., as shown in Fig. 5c for personal exposure monitoring of trichloroethylene with a GC-FID and the belt-mounted GC-sensor device\textsuperscript{167}) are rare.

Simpler implementation is achieved by focusing on single analytes for specific applications. An example is a detector consisting of a non-specific Pd/SnO₂ gas sensor and a compact separation column for screening of methanol in alcoholic beverages and exhaled breath to detect liquor adulteration and diagnose methanol poisoning non-invasively.\textsuperscript{68} The detector is handheld (94 g), fully integrated, inexpensive and can communicate results by Wi-Fi to a smartphone (Fig. 5d).\textsuperscript{175} It uses a compact packed bed (4.5 cm long, 4 mm diameter) of commercial Tenax TA sorbent with room air as carrier gas instead of a capillary or microchip GC column.\textsuperscript{68} As a result, methanol is detected selectively in the headspace of alcoholic drinks laced with 1 vol% methanol within 2 min (Fig. 5e).\textsuperscript{175} After flushing the column with room air for 10 min,\textsuperscript{68} it is fully regenerated and ready for the next measurement. The device revealed harmless from harmful concentrations of methanol.
down to 0.01 vol% in different wines, beers and liquors from six continents (Fig. 5f). This concept of simple packed bed separation columns can be adapted easily to other applications. For example, using a larger (500 mg) Tenax TA separation column, formaldehyde was measured within 2 min at concentrations as low as 5 ppb at 40% RH without interference by H₂, CH₄, CO, methanol, acetaldehyde, ethanol, and acetone. As a result, ppb-level formaldehyde concentrations were detected for the first time in wood-product emissions and in indoor air with a low-cost solid-state sensor. This is possible by the very high selectivity provided by the simple and modular packed bed sorption column, which cannot be reached typically by sensors alone (e.g., ZnO/ZIF-8 core–shell structures, NiO–SnO₂ microflowers) or their arrays (e.g., four SnO₂-based sensors).

3. Size-selective filters

Definitions & principles

Size-selective filters separate analytes by their kinetic diameter. These filters are microporous with pore sizes (usually <2 nm) comparable to analyte diameters. If applied as membranes in front of the sensor, analytes larger than the pore size are blocked (i.e., size cut-off) from reaching the sensor (Fig. 6a). This can result in very high selectivity to target analytes over hundreds of interferants typically present in such mixtures (e.g., VOCs in indoor air such as terpenes, alkenes, aromatic hydrocarbons). A drawback of such filters is their ineffectiveness for interferants smaller than the target analyte, which can be addressed by combination with other filter types or selective sensing materials. All size-selective filter–sensor systems are tabulated in Table 3 together with various figures of merit for comparison.

Most promising microporous materials are zeolites, MOFs and covalent organic frameworks (COF) featuring pore sizes that depend on crystal structure and composition. An advantage is the myriad of available frameworks (e.g., 248 zeolites, thousands of MOFs and COFs) offering distinct pore sizes that can be matched flexibly to target analytes. This is illustrated in Fig. 6b, showing the kinetic diameters of common analytes in gas sensing and the pore size of selected zeolites (red) and MOFs (blue).

The selectivity of such filters is characterized by the analyte permeance (molar flux per unit driving force). The permeance strongly depends on analyte size as shown in Fig. 6c exemplarily for a zeolite (SSZ-13) membrane with 0.38 nm pore size (dashed line). In fact, H₂ (0.28 nm) features almost three orders of magnitude higher permeance than SF₆ (0.55 nm). However, differences in adsorption strength between analytes can influence the permeance. For instance, CO₂ preferentially adsorbs on SSZ-13, hindering diffusion of other compounds in gas mixtures through the zeolite.

A key property of size-selective filters is their thickness that is inversely proportional to analyte permeance, as shown...
exemplarily for H₂ and He on 1.9–180 nm thick microporous graphene oxide (GO) layers (Fig. 6d). Thus, thin layers are needed for fast sensor responses. This often comes at the cost of higher defect density (e.g., cracks or pinholes), compromising separation selectivity since analytes can pass through the defects. The relation between defect concentration and diffusion is shown in Fig. 6e for propane and zeolite MFI membranes. Even extremely low defect concentrations reduce drastically analyte selectivity. Thus, a major challenge for effective size-selective filters is the synthesis of thin and defect-free ones (e.g., MOFs, zeolites and GO). Mixed matrix membranes (MMM) that consist of a microporous material dispersed in a polymer matrix are promising also. The MMMs can be easily processed to thin membranes with a small number of defects, resulting in high permeance while preserving selectivity.

Pore-size control

First size-selective filters were layers of amorphous SiO₂ directly on top of sensing films (e.g., SnO₂, Ga₂O₃, WO₃ or In₂O₃). These were obtained at elevated temperature (>500 °C) under exposure of the sensing film to a silicone source (e.g., hexamethyldisiloxane). The resulting microporous SiO₂ layer is impenetrable for most analytes except for very small H₂, resulting in a more than 100 times higher H₂ selectivity to VOCs (e.g., ethanol, acetone and benzene). This is remarkable for chemoresistive H₂ sensors, which offer low limit of detection (e.g., 10 ppb by CeO₂/In₂O₃) that is critical for leak detection, but typically suffer from poor selectivity (e.g., <13 to CO for that sensor). However, the introduced diffusion barrier also increased response and especially recovery times of sensors from seconds to several minutes depending on SiO₂ thickness. This is too long for most applications (e.g., seconds for leak detection).

Capitalizing on the effect of filter layer thickness on analyte permeance (Fig. 6d), SiO₂ layers with graded thickness had also been deposited on chemoresistive microarrays, allowing slight selectivity modulation from sensor to sensor. While individual sensors remain unspecific, different analytes (e.g., formaldehyde, CO, ammonia, acetone, etc.) were distinguished by pattern analysis in offline breath analysis and air quality monitoring. The pore size and shape of SiO₂ can even be adjusted flexibly by molecular imprinting of adsorbed molecules as template during deposition. For instance, templating such layers on SnO₂ sensors with benzaldehyde resulted in high selectivity to linear hexane over its branched isomers. However, templating with smaller butanal, however, reduced responses to all analytes.

Other microporous materials allow even more flexible control over pore size to adjust selectivity. For instance, pristine graphene oxide (GO) membranes have a narrow pore size distribution <0.3 nm that is typically adjusted (i.e., size and density) by physical (e.g., ion-bombardment) and chemical treatments (e.g., oxidative etching). Such dense and porous GO membranes with small (0.3–0.4 nm) and large (0.5–0.6 nm) pores were placed upstream of PdO/WO₃ sensors for selective detection of H₂S (Fig. 7a). The sensor with dense GO layer (Fig. 7b, squares) showed lower H₂S selectivity and sensitivity than the sensor alone (circles), as all analytes cannot pass the small intrinsic GO pores. For GO layers with large (triangles) and small (diamonds) pores, the H₂S selectivity is increased to formaldehyde and large analytes (i.e., ethanol, acetone and toluene) compared to the sensor alone. For instance, the selectivity to acetone is tripled (from 4.7 to 14) or even hours depending on SiO₂ thickness.
by covering the sensor with a GO layer having small pores, while response and recovery times did not change much. However, analytes smaller than the pore size (i.e., ammonia 0.29, H$_2$S 0.36 and methanethiol 0.45 nm) can pass through the pores more easily, so the H$_2$S selectivity is increased less. The exception is formaldehyde (0.23 nm), probably due to its preferential adsorption$^{221}$ on GO. Overall, the obtained H$_2$S selectivity is only moderate (<15 over ammonia and ethanol) and surpassed by other chemoresistive H$_2$S sensors (e.g., >700 over ammonia and ethanol by CuO$^{222}$). However, these modular GO layers could be combined readily also with other, more selective H$_2$S sensors.

Table 3  Size-selective filters in combination with gas sensors

| Filter configuration | Filter material | Target analyte | LOD$^a$ (ppm) | Response time | Tested interferants (selectivity) | Ref. |
|----------------------|----------------|---------------|----------------|---------------|-----------------------------------|------|
| Overlayer PMMA       | H$_2$          | Plasmonic     | 10             | <1 s          | CH$_4$ (63), CO$_2$ (32), CO (2.1), NO$_2$ (0.12) | 69   |
| SiO$_2$              | H$_2$          | SnO$_2$       | 20 000         | —             | Butane (>500), CH$_4$ (>500), CO (>500), ethanol (18), methanol (11) | 199  |
|                      |                |               | 50             | 60 s          | Acetone, benzene, ethanol (all >1000) | 203  |
|                      |                |               | 1000           | <1 min        | CH$_4$ (100), CH$_2$ (100), CO (>50), CH$_4$ (10), ethanol (10), methanol (10) | 209  |
|                      |                |               | 3100           | >1 min        | Acetone, CH$_4$, CO$_2$, ethanol, ethylene, propanol, NH$_3$, NO | 209  |
|                      |                |               | 0.250          | >1 h          | Acetone, CH$_4$, CO$_2$, ethanol, ethylene, propanol, NH$_3$, NO | 200  |
|                      |                |               | 500            | <30 s         | CH$_4$ (>100), isobutane (2), CO (6.8), ethanol (1) | 202  |
| MOF ZIF-8            | Formaldehyde   | ZnO           | 10             | 21 s          | Toluene (>100), acetone (10.6), ethanol (7.4), methanol (6.5), NH$_3$ (5.1) | 177  |
|                      |                | ZnO           | 10             | —             | Benzene (12), NH$_3$ (4.2), acetone (3.1), ethanol (2) | 181  |
|                      |                |               | 10             | >5 min        | Benzene, toluene (both $^a$) | 220  |
|                      |                |               | 5             | >5 min        | CO (37) | 227  |
| MOF ZIF-71           | H$_2$S         | WO$_3$        | 2             | 2 min         | Ethanol (19), acetone (11), NO$_2$ (3.4) | 230  |
|                      | H$_2$          | ZnO           | 20             | 29            | Acetone (1.9) | 234  |
|                      | Ethanol        | ZnO           | 50             | —             | Benzene, CH$_4$ (13), CH$_3$ (3.7), acetone (1.3), ethanol (2) | 181  |
| Zeolite FER CO       | La$_2$O$_3$-Au/SnO$_2$ | 0.050         | <1 min         | 1.7 min       | Acetone, CO$_2$, ethanol, H$_2$, NH$_3$ | 239  |
| Zeolite FER NO       | Zn$_{1.2}$-Cu$_{0.8}$O | 10            | 20             | 16 min        | CH$_4$ (>1000), propane (400), CO (100), H$_2$ (>100) | 236  |
|                     | Pd/SnO$_2$     | 10            | 0.50          | 21            | CH$_4$ (>1000), CH$_2$ (100), CO (200), propane (74), CO (35), H$_2$ (31) | 223  |
| Zeolite FER NO       | Zn$_{1.2}$-Cu$_{0.8}$O | 10            | 20             | 3 min         | H$_2$O (>1000), CH$_4$ (100), propane (83), CO (6.2), H$_2$ (2.2) | 223  |
| Zeolite FER NO       | Zn$_{1.2}$-Cu$_{0.8}$O | 10            | 21             | 5 min         | CO (100) | 238  |
| Zeolite FAU, BEA, MOR | Acetone, ethanol, NH$_3$, NO$_2$ | 1             | —             | —             | — | 240  |
| Mix. (LTA, FAU, MFI) | —              | SnO$_2$       | 2.5           | <5 min        | Acetone, butane, CO, ethanol, ethanol, isopropanol, propane, toluene | 241  |
| Overlayer SiO$_2$    | CO             | WO$_3$        | 100           | —             | — | 201  |
|                      | Acetone, CO, isopropanol | 0.5         | —             | — | 211  |
|                      | H$_2$S, NH$_3$ | WO$_3$        | 0.2           | >1 min        | Ethanol, H$_2$O | 212  |
| Indoor air contaminants | SnO$_2$, WO$_3$ | <1          | 5 s           | — | 213  |
| Overlayer SiO$_2$    | Alcohol, aldehydes, Hexane | SnO$_2$ | — | >1 min | 2,2-Dimethylbutane (>82), 2-methylpentane (82) | 215  |
| Membrane Graphene oxide | H$_2$S      | Pd/WO$_3$    | 1             | 30 s          | Acetone (14), NH$_3$ (14), formaldehyde (13), ethanol (11), toluene (11), methanol (4) | 219  |
|                     | Zeolite MFI    | Formaldehyde  | 0.03          | 8 min         | Ethanol (>1000), isopropene (>1000), methanol (>1000), NH$_3$ (>1000), acetone (>100) | 242  |

$^a$ Lowest measured concentration. $^b$ Not detectable by the sensor.
Zeolites and MOFs feature very narrow pore size distributions. While MOFs have been used as selective sensor materials (e.g., interference\textsuperscript{224}, or luminescent\textsuperscript{225}-based), the first implementation as auxiliary size-selective filters were ZIF-8 layers directly grown on ZnO nanowire sensors operated at 300 °C.\textsuperscript{220} The ZIF-8 membrane features pore openings of 0.34 nm\textsubscript{226} smaller than most analyte diameters (Fig. 6b). While the sensor without filter showed low (<5) H\textsubscript{2} selectivity to toluene and benzene, their responses are completely blocked by the ZIF-8 layer irrespective of their concentration, resulting in high H\textsubscript{2} selectivity. Using ZIF-8 as filter also blocked CO\textsubscript{227} ethanol\textsuperscript{228} and acetone.\textsuperscript{228} These results outperform even SiO\textsubscript{2}-covered sensors, especially as response and recovery times are unscauted due to the very thin (2–3 nm\textsuperscript{226}) ZIF-8 thicknesses. They are only outperformed by other sensor technologies such as optical nanoplasmonic sensors,\textsuperscript{229} which however typically suffer from higher detection limits (~100 ppm\textsuperscript{229}).

By using MOFs with different pore sizes, the selectivity can be changed drastically using the same sensor, as shown exemplary in Fig. 7c and d for MOF-coated ZnO nanorods.\textsuperscript{381} With ZIF-8 coating (Fig. 7d, yellow bars), most of ammonia and H\textsubscript{2} pass through, giving similar responses to bare sensors (red bars, reduced by <20%). The responses for larger analytes (i.e., ethanol, acetone and benzene), however, decreased by a factor of 4–6. In contrast, for ZIF-71 coatings with larger pore opening (0.48 nm, green bars), ethanol and acetone pass through and even show slightly higher sensor response than the uncoated sensor. Such increased responses were also observed for H\textsubscript{2}S on ZIF-71 covered WO\textsubscript{3} sensors\textsuperscript{230} and were attributed to enhanced analyte adsorption onto the ZIF-71.\textsuperscript{231}

Besides framework composition, the pore size of MOFs\textsuperscript{232} and zeolites\textsuperscript{233} can also be adjusted by encapsulation of ions or nanoparticles in their pores. For instance, the selectivity of a ZnO sensor coated with ZIF-71 was tuned by incorporation of silver nanoparticles.\textsuperscript{234} With increasing nanoparticle size and concentration, the response to acetone decreased by 64%, while that to H\textsubscript{2} increased by 83%.\textsuperscript{234} These results show how size-selective filters enable the control of sensor selectivity based on analyte size – otherwise impossible by sensor materials, arrays or other filter types that interact mostly chemically with the analytes.

Fig. 7e and f shows the effect of different zeolite frameworks on the selectivity of a Pd-doped SnO\textsubscript{2} sensor operated at 300 °C in dry air.\textsuperscript{223} MFI and LTA zeolite layers (~25 μm thickness with pore sizes 0.47 and 0.42 nm,\textsuperscript{107} respectively) were grown directly on screen-printed sensors (Fig. 7e) by seeding their surface with zeolite crystals and subsequent solvothermal synthesis.\textsuperscript{235} Fig. 7f shows the response with MFI (red bars) and LTA (blue bars) to different analytes normalized to the response without zeolite layer. While this sensor is non-specific, by adding an MFI layer, it responds selectively to H\textsubscript{2}, CO and H\textsubscript{2}O. In contrast, LTA increased primarily the selectivity to ethanol and H\textsubscript{2}O. Both layers significantly reduced the responses to propane and CH\textsubscript{4}, but also increased response times from 38 s to 16 min with LTA and MFI layers, respectively. The selectivity changes were mostly attributed to zeolite adsorption characteristics (LTA is hydrophilic and MFI hydrophobic) and not to size-selective diffusion, as the zeolite layers showed a large number of intra-crystalline voids (i.e., defects leading to unselective diffusion as shown in Fig. 6e). Layers with similar performance were prepared also by simple micro-dropping of zeolite suspensions directly on sensors to preserve their film integrity.\textsuperscript{236}
A variety of zeolites coated on different sensors (e.g., FER on Au–La$_2$O$_3$/SnO$_2$, LTA and MFI on WO$_3$, Cr$_2$TiO$_5$ and Zn$_{1-x}$Cu$_x$O$_2$ array of FAU, BEA and MOR on ZnO, array of LTA, FAU and MFI on SnO$_2$) showed a modulation of sensor response. For instance, ethanol selectivity over isopropanol of SnO$_2$ sensors was improved from 1.0 to 4.2 by covering with ~26 μm of MFI zeolite. However, the achieved selectivities were only moderate (<20), in the range typically observed for different sensor compositions without the need for filters and not yet suitable for low concentration analyte detection in complex mixtures (e.g., breath or indoor air). Furthermore, the selectivity improvements often cannot be attributed to size-selective filtering alone. In fact, they are often a complex interplay between (i) diffusion resistance, (ii) size-selectivity, (iii) preferential adsorption as a result of different filter surface properties (Section 2) and (iv) catalytic effects as a result of the thermal coupling of filter to the (typically) heated sensor (Section 4).

Filter configuration

Size-selective filters can be implemented as direct coatings (i.e., overlayer) or as membranes (free-standing or on a macroporous support) placed in front of sensors. Both configurations offer distinct advantages as shown here exemplarily with two filter–sensor systems for selective formaldehyde detection:

The first system uses a ZIF-8 MOF overlayer (~200 nm thick) directly formed on a ZnO sensor (Fig. 8a). While such coating of sensors with size-selective materials is attractive to maintain a compact sensor configuration, it leads to elevated filter temperature through its contact with the heated sensor (here 300 °C). This often degrades the size-selectivity as most microporous materials are catalytically active. The ZnO sensor without filter is mostly non-selective, giving high responses to a variety of analytes (Fig. 8b). With filter layer (Fig. 8c), responses to formaldehyde and ammonia, that are smaller than the ZIF-8 pores, are reduced only slightly. Also the sensor response times stay similar (14 to 21 s) because of the thin (~200 nm) filter layer. Large molecules such as toluene are blocked by the filter, resulting in pronounced formaldehyde selectivity >100, even in the presence of high humidity (>90% RH). However, other analytes larger than the pore size (i.e., methanol, ethanol and acetone) are not held back, probably because of catalytic conversion to smaller molecules on the heated ZIF-8 layer interacting with the ZnO. As a result, only moderate selectivities (5–11) are achieved that might be insufficient for measurement of formaldehyde in indoor air where interferant concentrations can be orders of magnitude higher. However, such size-selective ZIF-8 layers could be combined with other formaldehyde-selective sensors (e.g., In$_x$Sn$_{1-x}$O$_2$, NiO–SnO$_2$, Co/In$_x$O$_y$, or ZnO quantum dots loaded hollow SnO$_2$ nanospheres) or sensor arrays to further boost their selectivity. Alternatively, size-selective over-layers can be applied on room temperature sensors to avoid catalytic conversion of interferants.

In contrast, size-selective membrane filters can be produced individually with good control over morphology (e.g., thickness) and can be combined as separate units more flexibly with sensors (e.g., electrochemical, optical). Fig. 8d–f shows an example where a size-selective membrane of MFI zeolite was formed on a macroporous Al$_2$O$_3$ support (Fig. 8d) and placed upstream of a Pd-doped SnO$_2$ sensor. Similar to uncoated ZnO, the Pd-doped SnO$_2$ sensor (Fig. 8e) alone is not selective. In contrast to the overlayer, however, the membrane features a size-cutoff, as analytes larger than the pore size (i.e., isoprene and TIPB) are barely detected by the sensor (Fig. 8f). Interestingly, also smaller analytes (i.e., methanol, ethanol, acetone and ammonia) are blocked effectively by the membrane, probably as a result of adsorption effects. So, excellent formaldehyde selectivity up to more than 1000 is
achieved even at low concentrations down to 30 ppb at 90% RH, unmatched by most chemoresistive sensors. A drawback of this configuration, however, is the larger zeolite thickness (~3 μm) that introduces a high diffusion resistance. As a result, the formaldehyde response is reduced by a factor of 5 and the response and recovery times increased to 8 and 72 min, respectively, significantly higher than those with overlayers (Fig. 8a–c).177

4. Catalytic filters
Definitions & principles
Catalytic filters exploit differences in chemical reactivity between analytes to enhance the selectivity of downstream sensors. Ideally, the target analyte passes the filter intact, while interferants convert fully on the filter (catalyst) to inert species undetected by the sensor, as illustrated in Fig. 9a. Nevertheless, partial analyte conversion and formation of intermediates has been observed.249 As a result, interferants are eliminated or their concentration is reduced substantially, resulting in high sensor selectivity. Most importantly with respect to other filters, catalytic ones operate continuously (and do not saturate like sorption filters, Section 2). This is a distinct feature if interferants are present constantly in the background air (e.g., ethanol from cleaning products or disinfectants). However, catalytic filters usually require some heating to optimize selectivity, which can be circumvented if the catalytic filter is deposited directly onto the heated sensing film as an overlayer.

![Chemical reaction pathways between analytes and catalytic filter](image)

**Fig. 9** (a) Chemical reaction pathways between analytes and catalytic filter. Analytes thereby pass the catalyst unscathed without reaction (desired for the target analyte) or are converted to intermediate or inert species (desired for interferants). (b) Increased noble metal loading lowers filter temperature for complete conversion.252 (c) Increased RH253 and (d) analyte concentration254 increases that temperature.

A variety of crystalline or amorphous catalytic materials is available from heterogeneous catalysis, including metal oxides, mixed-metal catalysts, zeolites, mesoporous silica and MOFs. They typically feature high specific surface areas (e.g., > 100 m² g⁻¹) with surface composition, structure and operational temperature determining the overall reactivity, and subsequently, selectivity. These properties make catalytic filters attractive for material engineering at the nanoscale (e.g., surface area, acidity or surface hydrophobicity). In particular, noble metals (e.g., Pt, Pd, Rh, Au and Ag) are frequently added to enhance reactivity by tuning their size down to single atoms. For example, increasing the loading of Pt on Al₂O₃ from 0.5 (triangles, Fig. 9b) to 1.5 wt% (squares) reduces the temperature of full propene combustion from 160 to 100 °C.

In contrast to heterogeneous catalysis, catalytic filters for sensors are typically operated in mixtures with many compounds (e.g., several hundred in human breath), low analyte concentrations and high or varying humidity. These parameters markedly influence the reactivity and selectivity of catalytic filters. For example, catalyst activity is strongly influenced by humidity as water molecules can competitively interact and block catalytic active sites, reducing their reactivity. As an example, the onset of CH₄ conversion on Pd/SnO₂ shifts from 240 °C in dry air to 320 °C at just 10% RH (Fig. 9c). For sensor applications, humidity often varies greatly (e.g., 30–95% RH in indoor air) or is present at high levels (e.g., exhaled breath > 97% RH), which needs to be considered in the design of catalytic filters. Furthermore, analyte concentration influences conversion at high concentrations when the reaction kinetics (i.e., diffusion to, adsorption on, conversion at and desorption from the catalyst) become rate-limited. For instance, on Pt/Al₂O₃–CeO₂, complete conversion of 1000 ppm toluene is attained at 250 °C, while for 3600 ppm it is 300 °C (Fig. 9d).

For gas sensors, the catalytic filter needs to convert interferants at high concentrations and leave intact the target analyte often present at orders of magnitude lower concentration (e.g., < 10 ppb formaldehyde in indoor air with > 10 ppm H₂, ethanol or acetone). So, heterogeneous catalysis can inspire the design of catalytic filters, but their performance needs to be tailored systematically to sensor conditions.

**Tailored selectivity**
Sensors with catalytic filters are tabulated in Table 4, showing their composition, target analytes and various figures of merit. First catalytic filters for gas sensors were developed to remove VOCs (e.g., CO and ethanol) for reliable alkane detection. Monitoring alkanes (e.g., CH₄, propane and butane) in indoor air and industrial areas (e.g., from gas leaks and coal mines) is important due to their high flammability and regulated exposure limit. (e.g., CH₄, 1000 ppm) is challenging, as chemoresistive sensors respond weakly to alkanes (high energy needed to activate C–H bonds) and suffer from high cross-sensitivity to pollutants, particularly CO (e.g., > 7000 ppm in coal mines and > 100 ppm in industrial areas) and ethanol (e.g., > 100 ppm from hand disinfection).
Table 4  Catalytic filters in combination with gas sensors

| Filter configuration | Filter material | Target analyte | Sensor | LOD* (ppm) | Response time | Tested interferants (selectivity) | Ref. |
|----------------------|-----------------|----------------|--------|------------|---------------|---------------------------------|------|
| Overlayer            | Al₂O₃           | CH₄            | Pellistor | 25 000     | —             | Hexamethyldisiloxane (<1)       | 59   |
|                      | Co₃O₄           | Benzene        | Pd/SnO₂  | 0.25       | 3 s           | Ethanol (5.1), xylene (4.8), toluene (2.6), CO (2.4), formaldehyde (2.4) | 300  |
|                      | CuO             | CO             | SnO₂     | 900        | —             | Ethanol (<1)                     | 308  |
|                      | Cr₂O₃           | Ethylene       | SnO₂     | 0.1        | 9 s           | NH₃ (24), dimethylamine (17), formaldehyde (6.3), ethanol (5.7), CO (4.3), trimethylamine (3.4) | 312  |
|                      | Ga₂O₃           | CH₄            | Ga₂O₃    | 500        | —             | Ethanol (2), acetone (<1)       | 286  |
|                      | Zeolite MFI     | CO             | Pd/WO₃   | 100        | —             | Acetone, ethanol, methanol (all <1) | 305  |
|                      | SnO₂, TiO₂      | Toluene, xylene| Co₃O₄    | 5         | <6 min        | Formaldehyde (>20), CO (>10), benzene (>8), ethanol (>7.6) | 303  |
|                      | Pt               | CO             | SnO₂     | 10         | —             | NO₂ (<1), ozone (<1)            | 310  |
|                      | Pd               | Propane        | In₄₀.₃Sb₀₃₀.₀₆₆₆Pd₀₁/ SnO₂ | 500 | — | CO (>1000), ethanol (1) | 73   |
|                      | Pd, Ag           | CO, H₂         | SnO₂     | 1000       | <3 min        | Oxide (<1)                      | 307  |
|                      | Pt/Al₂O₃        | CH₄, ethanol   | SnO₂     | 100        | —             | CO (>1000), ethanol (>20), benzene (>10), acetone (>5) | 250  |
|                      | Pt & Pd/SiO₂     | Benzene        | WO₃      | 1          | —             | Ethanol (5.8), NH₃ (<1), NO₂ (<1) | 301  |
|                      | Pt/zeolite       | Propane        | SnO₂     | 200        | —             | CO (>1000)                      | 278  |
|                      | MFI              | Methanol       | Pd/WO₃   | 2          | —             | CO (>1000), ethanol (13), acetone (8) | 305  |
|                      | Pd/Al₂O₃        | CH₄, butane, propane | SnO₂, InO₂ | 10 000 | — | CO, ethanol | 51 |
|                      | SiO₂, WO₃       | CH₄            | Pd/SnO₂  | 50         | —             | CO (>1000), ethanol (1)         | 283  |
|                      | Pd/SnO₂         | CO, CH₄        | SnO₂     | 100        | <100 ms       | CO (10), H₂ (5)                 | 284  |
|                      | RuO₂/SiO₂       | CO             | SnO₂     | 300        | —             | Ethanol (1)                     | 287  |
|                      | Mo/zeolite Y     | Heptane, octane| Cr₃₋ₓTeₓO₅ₓ | 150   | —             | NO₃ (5), CO (2.75)              | 282  |
|                      |                  |                | Si/WO₁   | 0.25       | —             | Nonane (1), decane (2), undecane (3) | 309  |
| Packed bed           | ZnO              | Acetone, benzene, H₂, CH₄, toluene | Si/WO₁ | 0.25 | — | Ethanol (81), formaldehyde | 294 |
|                      | Au/              | CH₄            | Pt/SnO₂  | 5000       | 35 s          | Acetone, CO, ethanol, formaldehyde, toluene (all >100) | 288 |
|                      | Ce₀.₅Zr₀.₅O₂     | CH₄            | Pt/SnO₂  | 2000       | 10 s          | CO, ethanol (both >1000)         | 291  |
|                      | Au/Fe₃O₄        | CH₄            | Pt/SnO₂  | 100        | —             | CO (2.1)                        | 292  |
|                      | Au/TiO₂         | Propane        | SnO₂     | 100        | —             | CO (7.4)                        | 292  |
|                      | Au/ZnO          | Propane        | SnO₂     | 100        | —             | CO (1000), isoprene (>1000), NH₃ (>1000), ethanol (>500), H₂ (>250) | 70   |
|                      | Pt/Al₂O₃        | Acetone        | Si/WO₁   | 0.05       | 55 s          | CO (>1000), NO (>100)           | 306  |
|                      | Pt/Al₂O₃        | Propane        | Pt/SnO₂  | 1000       | 30 s          | CO (1000), NO (>100)            | 306  |

* Lowest measured concentration.

Typical catalysts consist of noble metals (e.g., Pt, Pd and Au) on ceramic supports (e.g., Al₂O₃, SiO₂ and Fe₂O₃) that are deposited directly onto sensing films as porous layers. Their working principle is illustrated in Fig. 10a on the example of a SnO₂ sensor (operated at 350 °C) covered by a layer (100–150 μm) of mesoporous Pt or Pd/SiO₂. Without filter (Fig. 10b), the sensor shows similar resistance changes (i.e., responses) to 20–400 ppm CO (dashed line) and 200–4000 ppm CH₄ (solid line), typical for such SnO₂-based sensors. With filter, CO is fully converted in the filter layer to non-responsive species (i.e., CO₂, H₂O) while chemically stable CH₄ passes unscathed. As a result (Fig. 10c), no resistance changes to CO are detected anymore, while they are unchanged for CH₄, resulting in selective CH₄ detection. Such CH₄ sensor systems outperform sensors without filter (e.g., methane to CO selectivity of 8 for Pd–Ag activated ZnO²⁷⁹ and ZnO/ZnO₂ heterostructures²⁸⁰) and enabled industrial development of selective gas leak sensors to prevent false alarms²⁸¹.

A variety of catalysts appear suitable for this application, as similar results were obtained with several Al₂O₃- and SiO₂-based catalysts (e.g., thermally evaporated pure Al₂O₃ and SiO₂,²⁸³ drop-coated Pt,²³ Pd²³ and RuO₂²⁸² on SiO₂,²³ flame deposited Pd/Al₂O₃²⁸³ and screen printed Pt/Al₂O₃,²⁵⁰ Pd/Al₂O₃,²⁸⁴ and Pt/ZSM-5 zeolites²⁸⁵, Ga₂O₃,²⁸⁶ WO₃,²⁸³ Pd/SnO₂,²⁸⁷ and Au/ Ce–Zr.²⁸⁸ The preferential conversion of VOCs over alkanes is expected due to the alkane’s higher chemical stability.²⁸⁹ Disadvantages of such filters are their limited applicability to alkane detection, as well as typically high operation temperatures (i.e., > 350 °C).²⁷⁸ However, the performance of filters can be improved further and their selectivity tuned more flexibly by exploiting specific analyte-catalyst interactions. For instance, gold catalysts are highly active and selective to CO₂ and more stable than Pt catalysts.²⁸⁹
reactive to CO already at room temperature. In fact, catalytic filters such as Au/Fe$_2$O$_3$, Au/ZnO, and Au/TiO$_2$ removed CO selectively over alkanes (e.g., propane) even at room temperature, with the highest removal efficiency in the order of Au/Fe$_2$O$_3$ > Au/ZnO > Au/TiO$_2$.

More challenging are filters that distinguish between VOCs with similar stability (e.g., ketones, aldehydes, aromatics), requiring more precise material engineering. For instance, high ethanol background in ambient air or breath ( > 100 ppm from disinfectants and alcohol consumption) is a common issue preventing accurate measurements of target analytes. This was addressed by a catalytic filter that exploits surface acidity and basicity (Fig. 11) for selective measurement of acetone, a metabolic breath marker for fat oxidation. The acetone carbonyl group coordinates primarily with Lewis acid sites abundantly present on acidic oxides (e.g., WO$_3$). In contrast, ethanol conversion is favored on basic oxides (e.g., CH$_4$) pass through the filter unscathed and are detected by the sensor, while interferants (e.g., CO) are converted to non-responsive species (e.g., CO$_2$). Reproduced with permission. Copyright 2003 Elsevier. SnO$_2$ sensor response to CO (20–400 ppm, dashed line) and CH$_4$ (200–4000 ppm, solid line) without (b) and with (c) a Pd/SiO$_2$ mesoporous catalyst filter at 30% RH.

Fig. 10 (a) SEM cross-section of a SnO$_2$ sensor with a mesoporous catalytic overlayer (filter). Alkanes (e.g., CH$_4$) pass through the filter unscathed and are detected by the sensor, while interferants (e.g., CO) are converted to non-responsive species (e.g., CO$_2$). Reproduced with permission. Copyright 2003 Elsevier. SnO$_2$ sensor response to CO (20–400 ppm, dashed line) and CH$_4$ (200–4000 ppm, solid line) without (b) and with (c) a Pd/SiO$_2$ mesoporous catalyst filter at 30% RH.

Intoxicated volunteer through such a small (150 mg) packed bed filter of ZnO heated to 260 °C completely eliminates ethanol interference (Fig. 11e). Most importantly, the filter leaves acetone intact as verified by responses of a Si/WO$_3$ sensor without and with filter (Fig. 11f) and confirmed by benchtop mass spectrometry. Ethanol responses are strongly reduced (i.e., by 88% at 20 ppm ethanol, remaining response from the combustion to H$_2$O), resulting in selective acetone detection down to 25 ppb in breath-relevant 90% RH with a selectivity to ethanol of 81. This ZnO filter fully combusts also other interferants (e.g., formaldehyde), while leaving aromatics (e.g., toluene, benzene), CH$_4$ and H$_2$ intact. The selectivity can be further increased by removing the ethanol conversion products (i.e., H$_2$) by other (catalytic) filters or by operating the filter at higher temperature, although this can reduce the sensitivity by partially converting the target analyte (i.e., acetone).

Catalytic filters can even increase selectivity to analytes from the same chemical group. For instance, the selective detection of carcinogenic benzene over toluene and xylene in indoor air is challenging for chemical gas sensors due to the chemical similarity of these analytes (aromatic hydrocarbons with 0–2 methyl groups). A promising approach is the use of catalytic Co$_3$O$_4$ overlayers electron-beam evaporated onto Pt/SnO$_2$ sensing films. Toluene and p-xylene were partially converted in the filter layer to non-reactive species, reducing their responses by as much as 97%, depending on Co$_3$O$_4$ thickness (0–60 nm). In contrast, the response to benzene increased by 30% at optimal filter thickness (20 nm), attributed to its activation in the catalytic layer through formation of more responsive intermediates, as has been observed for benzene detection already with Pt/Al$_2$O$_3$ filters. As a result, benzene selectivity to p-xylene, toluene, ethanol, formaldehyde and CO was doubled from ~1 to >2 that could be further improved with sensors featuring intrinsic benzene selectivity (e.g., Au/multi-walled carbon nanotubes with benzene selectivity towards o-xylene and toluene > 30). Most interesting, by switching the filter–sensor arrangement, i.e., Co$_3$O$_4$ was used as sensor with a catalytic filter layer of SnO$_2$, also the selectivity could be reversed. Toluene and p-xylene responses increased up to a factor of 5 (possibly through formation of more responsive benzy alcohol), while responses of interferants decreased significantly. As a result, toluene and p-xylene selectivity > 20 could be achieved towards benzene, ethanol, formaldehyde and CO.

Similarly, increased selectivity through higher sensitivity to target analytes was observed also for other catalytic filters. For instance, a Pd/WO$_3$ sensor covered by undoped zeolite layers (HZSM-5) increased the CO response by a factor of 7 resulting in selectivity of more than 4 over methanol, ethanol and acetone. Covering the same sensor with Pt/HZSM-5 increased methanol responses by a factor of 15 resulting in selectivity > 9 over the same analytes. Packed bed filters of Pt/LaFeO$_3$ heated to 200 °C upstream of Pt/SnO$_2$ sensors turned selective to CO with negligible interference from propane. However, when operating the filter at 350 °C, sensor responses to propane increased by a factor of 25 while CO was completely
removed. Also, nanolayers (5–20 nm) of Pd or Ag deposited by successive ionic layer deposition on SnO$_2$ sensors removed ozone interference and increased responses to reducing gases (e.g., CO and H$_2$).\textsuperscript{307} While such catalytic filters offer a powerful tool to enhance sensitivity and tailor selectivity, none of these studies investigated the composition of the effluent, to identify the reformed species and characterize their interaction with the sensor, motivating further research.

**Filter configuration**

Catalytic filters are typically deposited directly\textsuperscript{283} as overlayers (e.g., as porous layers,\textsuperscript{281} membranes,\textsuperscript{309} zeolite\textsuperscript{309} or metallic nanoclusters\textsuperscript{116}) onto sensor materials. This results in compact filter–sensor systems where sensing film and catalyst temperature are coupled, requiring no additional heating source. However, this also implies that filter and sensor cannot be fabricated and operated individually to achieve maximum selectivity. Additionally, overlayers may act as diffusion barrier, increasing response times (e.g., from 1 to 4 min for 20–70 \textmu m thick zeolite layers on SrTi$_{1-x}$Fe$_2$O$_{3-δ}$ sensors).\textsuperscript{311} While depositing thin\textsuperscript{112} or highly porous\textsuperscript{278} catalytic overlayers can address this, filter efficiency could be compromised. Finally, solid-state diffusion of the catalytic layer into the sensing film may alter sensor performance (e.g., catalytic Pd diffusion into SnO$_2$ sensor).\textsuperscript{287} This can be solved by an additional inert separation layer (e.g., Al$_2$O$_3$\textsuperscript{108} or SiO$_2$\textsuperscript{73}).

Such a SnO$_2$ gas sensor (operated at 375 °C) with a Cr$_2$O$_3$ catalytic overlay deposited by electron-beam evaporation had been tested as ethylene sensor (Fig. 12a–c).\textsuperscript{312} Ethylene monitoring is used for controlling growth, development and ripening of fruits.\textsuperscript{513} Fig. 12a shows a cross-section SEM image of the Al$_2$O$_3$ substrate, the SnO$_2$ sensing layer (∼21 \textmu m) and a thin Cr$_2$O$_3$ overlayer (300 nm). Without the Cr$_2$O$_3$ overlayer, the SnO$_2$ sensor features high sensitivity to ethylene, but responds also to trimethylamine (TMA), dimethylamine (DMA), ammonia (NH$_3$), ethanol, formaldehyde (HCHO) and CO (Fig. 12b). With this catalytic overlayer, the responses to all interfering analytes are reduced, while the ethylene response remains similar. As a result, ethylene selectivity to the tested analytes increases from 1–3.8 to 3.4–24 with an estimated ethylene limit of detection of only 24 ppb. Increasing the Cr$_2$O$_3$ layer thickness (from 300 to 600 nm) further reduces responses to interferants but also to ethylene, resulting in overall poorer selectivities. The filter–sensor system was further integrated into a hand-held device with wireless communication, which monitored fruit ripening (exemplarily shown for a banana in Fig. 12c) under controlled conditions (i.e., in a closed chamber). While promising, further validation with a high-resolution instrument (e.g., GC-MS) and testing in indoor air is required.

Catalytic filters can be implemented also as packed beds upstream of the sensor affording individual optimization and operation, as well as flexible combination with different sensors (e.g., chemoresistive, electrochemical or optical). A drawback is the sometimes necessary additional heating source\textsuperscript{294} and pressure drop when air is drawn through the filter to the sensor by a pump.\textsuperscript{314} The former can be addressed by tailoring materials at the nanoscale (e.g., introducing highly reactive noble metals\textsuperscript{290}). Such a compact (30 mg) catalytic packed bed filter of Pt/Al$_2$O$_3$ nanoparticles had been used for a selective breath acetone sensor (Fig. 12d–f).\textsuperscript{70} Acetone is a breath marker for fat metabolism\textsuperscript{295} with applications in personalized exercise\textsuperscript{315} and diet monitoring,\textsuperscript{316} as well as search and rescue.\textsuperscript{317} While Pt/Al$_2$O$_3$ is used already to remove VOCs over alkanes, tailoring the Pt-loading is necessary to allow

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**Fig. 11** (a–d) Conversion of 1 ppm ethanol (triangles) and acetone (circles) on metal oxides with increasing basicity, WO$_3$ < SnO$_2$ < Fe$_2$O$_3$ < ZnO, that increases the acetone selectivity over ethanol. (e) Ethanol concentration measured during three consecutive breath exhalations without filter (t ≤ 3 min) and with 150 mg ZnO filter at 260 °C (t > 3 min) that totally eliminated ethanol. (f) Si/WO$_3$ sensor response to 1 ppm acetone and 5, 10 and 20 ppm ethanol without (open bars) and with a ZnO catalyst at 260 °C (filled bars) upstream of the sensor.\textsuperscript{294}
for selective combution of breath-relevant interferants over acetone. For example, 0.2 mol% Pt/Al2O3 removed selectively isoprene, alcohols, aldehydes, aromatics, CO, H2 and NH3 over acetone with high robustness to humidity (30–90% RH) at 135 °C. Fig. 12d shows the crystalline Al2O3 particles decorated with 0.2 mol% Pt clusters (average size 9 nm).70 When coupled to a Si/WO3 sensor, this results in unprecedented acetone selectivity (>250, Fig. 12e), which cannot be achieved by sensors alone (e.g., selectivity to ethanol <10 by Si/WO3 and isoprene <4 by Al/ZnO3) or orthogonal sensor arrays.48

Most importantly, the sensor exhibits sufficiently low limit of detection (i.e., 5.5 ppb that is superior even to 30 ppb by more bulky GC-IMS319), and the response time is not affected by the filter (i.e., 1.3 min at 100 ppb). For validation, breath samples after exercise were analyzed by the filter–sensor system and simultaneously with benchtop mass spectrometry (Fig. 12f). The sensor correctly detects the increase of breath acetone indicating fat combustion, in excellent agreement with the benchtop method and is applicable also in extreme scenarios (i.e., in presence of alcohol disinfectants as well as >50 ppm H2 and CH4 in exhaled breath320). Such filter–sensor systems can be implemented readily in commercial and portable breath analyzers.321

5. Conclusions and outlook

Today, many commercial sensors already use filters in specific applications (e.g., catalytic and sorption filters in CO66 and CH4,67 alarm sensors or GC columns for detection of H2 and CH4 in breath152). Furthermore, a plethora of next generation sensor technologies and advanced sensing materials are available with impressive performance in the laboratory. To fully assess their potential, they need to be validated under realistic conditions (e.g., detection of pollutants in indoor air322 or markers in exhaled breath141). In fact, today most commercial chemical sensors fail in such emerging applications as they lack the required selectivity.

Filters help single sensors and sensor arrays to overcome selectivity limitations as had been shown already for selective detection of CO86 and a variety of VOCs (e.g., methanol,68 isoprene,71 formaldehyde,176 trichloroethylene,167 etc.) by sorption filters, H269 and formaldehyde242 by size-selective filters, and alkanes (e.g., CH4,67 and propane292) and acetone70 by catalytic filters. Selectivity tuning with filters can be achieved by exploiting a variety of molecular properties of analytes, including molecular size, surface affinity, diffusion properties and chemical reactivity. These are typically not accessible by the sensor alone, which is focused on reactivity (i.e., chemoresistive sensors), electromagnetic absorption (i.e., optical sensors), or molecular mass (i.e., quartz microbalances). By tuning filter selectivity by material design and combination of filters with suitable sensors, an array of new and promising applications is unlocked.

For instance, a handheld methanol detector enabled by a sorption filter can detect methanol-adulteration in drinks,173 responsible for thousands of victims every year. Such detectors...
can also be used to monitor naturally occurring methanol during liquor distillation (e.g., fruit spirit or whisky), detect methanol in the breath of methanol poisoning victims to initiate immediate and appropriate treatment with better chance of recovery, and detect the presence of methanol in sanitizers, responsible for >700 deaths in Iran and USA during the recent COVID-19 pandemic. Even screening for COVID-19 by a quick breath test might be possible after recent research suggested methanol as one of the tentative breath markers of the disease. Or, a sensor enabled by a catalytic filter can selectively detect acetone in the breath. Integrated into a simple-in-use, portable detector, it enables for the first time for the detection of formaldehyde in indoor air. Given the immense potential of filters, they will almost certainly play a pivotal role in the future development of advanced sensor systems with unprecedented selectivity as they have done already for CO and CH₄.

These examples demonstrate how filters drastically increase the selectivity of sensors to meet demanding requirements in emerging applications. This results in useful devices with immediate societal impact. Other examples include sensors for food quality control (e.g., monitoring ethylene during fruit ripening) and air quality monitoring (e.g., fast measurement of formaldehyde in indoor air). Given the immense potential of filters, they will almost certainly play a pivotal role in the future development of advanced sensor systems with unprecedented selectivity as they have done already for CO and CH₄.

Conflicts of interest
The authors report no declarations of interest.

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