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Selective Detection of NO_2 with Specific Filters for O_3 Trapping †

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Abstract: The present study evaluates the ozone (O_3) and nitrogen dioxide (NO_2) removal performance of specific filters based on nanoporous materials. These materials, produced via the sol-gel process with functionalized silicon alkoxides as precursors, are tailored for O_3 trapping. The gas removal effectiveness of the filters was assessed through measurements of O_3 concentrations in the air upstream and downstream of the filters. Depending on the filter nature, O_3 can be totally trapped while NO_2 can pass over a specific concentration range.

Keywords: selective filter; gas sensors; trapping efficiency; ozone; nitrogen dioxide

1. Introduction

The Tropospheric or ground level ozone (O_3) is an air pollutant produced by photochemical reactions and chemical reactions between oxides of nitrogen (NO_x) and volatile organic compounds (VOC). High outdoor O_3 concentrations have been linked to asthma exacerbation, respiratory symptoms, heart attacks and premature death. In addition to the direct health risks, O_3 can also chemically react with various indoor pollutants [1,2] to produce more toxic volatile compounds. Since O_3 is the main interfering pollutant for NO_2 monitoring in the context of air quality control, various filters (nanocarbon, indigo thin film or MnO_2) were proposed and were found to efficiently trap O_3 without trapping NO_2 [3,4]. However, due to their structure, these filters were found to be too short-lived. Thus, our approach consists in the implementation of a relevant chemical filter highly impervious to O_3 and weakly reactive with NO_2 placed upstream a MOX gas sensors.

Various filters have been investigated based on several functionalized nanoporous materials doped with indigo carmine for the selective trapping of O_3. The filtering efficiency towards the target gases have been experimentally quantified for the different gas concentrations.

The work presented in this paper is divided into two parts; firstly, we describe the strategy of producing various filters with functionalized nanoporous matrices via the sol-gel process. Then, the synthetized filters will be tested in order to quantify their ability of O_3 trapping under various conditions. The second part is dedicated to the selection of filters to be used for NO_2 detection in O_3 environment. Various tests have been performed to check the total O_3 trapping by the filters with sensor and NO_2 detection with WO_3 based gas sensor using various O_3 up-stream filters.

2. Experimental

2.1. Syntheses of Doped Nanoporous Matrices and Characterization

Nanoporous monoliths of hybrid organic-inorganic polymers doped with indigo carmine were prepared via the Sol-Gel method using as reactants one or two silicon precursors. A one-pot synthesis procedure is applied for all syntheses. The chosen silicon precursors are tetramethoxy silane (TMOS), phenyl-triethoxysilane (PhTEOS) and chloropropyl-trimethoxysilane (ClTMOS). TMOS or a mixture of TMOS with either PhTEOS or ClTMOS are added to the solvent, MeOH, in a beaker and the mixture is vigorously stirred while adding an aqueous solution of indigo carmine. The concentration of indigo carmine in the aqueous solution, 70 $g \cdot L^{-1}$, corresponds to its solubility in water. The sol was poured into specific molds where gelation occurs. The gels were dried in a desiccator under a N_2 stream at room temperature. After the shrinkage process, transparent and dark blue monoliths were obtained. The proportion of the reactants is given in Table 1 along with the drying time.

Table 1. Synthesis conditions and porosity properties of the matrices doped with indigo carmine (IC). [IC] corresponds to the concentration in the Sol.

Filter	Sol Composition Molar Proportion	[IC] $mol \cdot L^{-1}$	Drying Time Days	Sads $m^2 \cdot g^{-1}$	V3 $cm^3 \cdot g^{-1}$
F1	TMOS/PhTEOS/MeOH/H_2O 0.85/0.15/4/4	0.0266	38	560 ± 50 34% (11–20 Å), 66% (21–53 Å)	0.38 ± 0.01
F2	TMOS/ClTMOS/MeOH/H2O 0.8/0.2/4/4	0.0271	38	8 ± 2 100% (25–70 Å)	0.01
F3	TMOS/ClTMOS/MeOH/H_2O 0.5/0.5/4/4	0.0263	32	Non porous	-
F4	TMOS/ClTMOS/MeOH/H2O 0.7/0.3/4/4	0.0304	15	Non porous	-

The concentration of indigo carmine in the final matrices varies from 0.280 to 0.324 $mol \cdot cm^{-3}$, depending on the formulation. The porosity parameters, specific adsorption surface area and pore volume were determined via collecting adsorption isotherms of N_2 at liquid nitrogen temperature with a porosity analyzer, Autosorb-1 from Quantachrome Instruments. F1 displays the highest specific adsorption surface area due to the presence of 34% of micropores (diameter < 20 Å) while F2 displays only mesopores (500 > diameter > 20 Å). The materials listed in Table 1 are ground, sieved and transferred into syringes of 3 mm of diameter. Each filter is filled with 1.79 g of the material to be tested.

2.2. Experimental Set-Up for the Detection of O_3 and NO_2

The sensor used in this study consists of a new microhotplate platform and a sensitive layer. The microhotplate architecture was initially developed by IM2NP laboratory [5]. A thin dielectric membrane of 450 μm × 430 μm supports a set of three sensors and two heaters. A platinum heaters was designed to ensure the optimum response of the sensitive layer (Figure 1). In addition, two pairs of Pt electrodes were deposited on the same mask level and used to recover the signal on the sensitive layer. The metal-oxide is a polycrystalline WO_3 sensitive layer (50 nm thick) produced by reactive R.F (13.56 MHz) magnetron sputtering and can detect both O_3 and NO_2. The gas sensing response is obtained by measuring the microsensor resistance with a Keithley 2450 source meter. The sensor is placed in a close thermo-regulated test chamber. The sensor sensitivity to NO_2 and O_3 is studied under several pollutant concentrations, from 200 ppb to 1000 ppb for NO_2 and from 36 ppb to 210 ppb for O_3. The experimental setup allows the tests of sensors under dry air and various calibrated gas mixtures, without or with the up-stream filter. For each pollutant concentration, the sensor was exposed to the gas mixture with constant flow rate of 500 sccm.

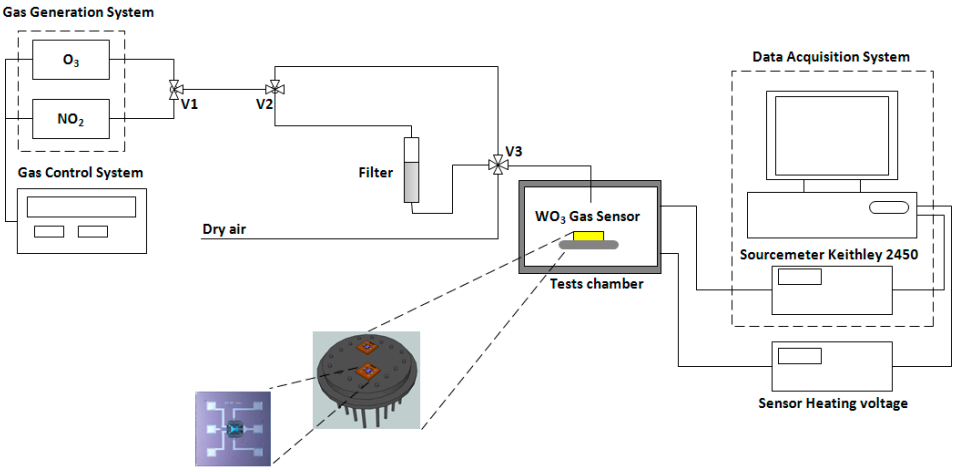

Figure 1. Experimental setup for gas sensors and filters tests.

The trapping efficiency, τ, corresponds to the amount of gas removed and is expressed in % (Equation (1)). τ is measured for each filter as a function of the exposure parameters.

$$\tau = \frac{[gas]_{up} - [gas]_{down}}{[gas]_{up}} 100\% \quad (1)$$

3. Results and Discussion

In order to evaluate the efficiency of O_3 and NO_2 trapping, different measurements were carried out for each filter filled with 1.79 g of filtering material and placed up-stream of the WO_3-based sensor. F1 and F2 filters were found to remove completely O_3 but not NO_2 as shown in Table 2. In contrast, F3 and F4 which display no porosity only partially remove O_3 and NO_2.

Table 2. Filter trapping performance under O_3 and NO_2.

Filter	O_3	NO_2
F1	✓	×
F2	✓	×
F3	×	×
F4	×	×

✓: removes completely the gas molecules; ×: does not completely remove the gas molecules.

The efficiency of the filters in removing O_3 is further tested with reduced amounts of filtering material (0.2 g). As shown in Figure 2a, F1 and F2 can still completely eliminate O_3 molecules while only a part of the initial concentration is removed with F3 and F4. For these latter, it can also be noted that the O_3 removal is increased with increasing O_3 concentration. In other terms, this means that the O_3 amount passing through the filter decreases as the up-stream concentration O_3 increases.

On the other hand, and unlike the O_3 case, all the filters remove partially NO_2 as illustrated in Figure 2b and the NO_2 removal appears to be dependent on the up-stream NO_2 concentration.

These preliminary results clearly indicate that F1 and F2 can efficiently trap O_3 and could be used to measure NO_2 in gas mixtures containing both pollutants. Further experiments will be needed to find out the range of NO_2 concentration over which F1 and F2 could be used up-stream of the sensor for the measurements of NO_2 in air.

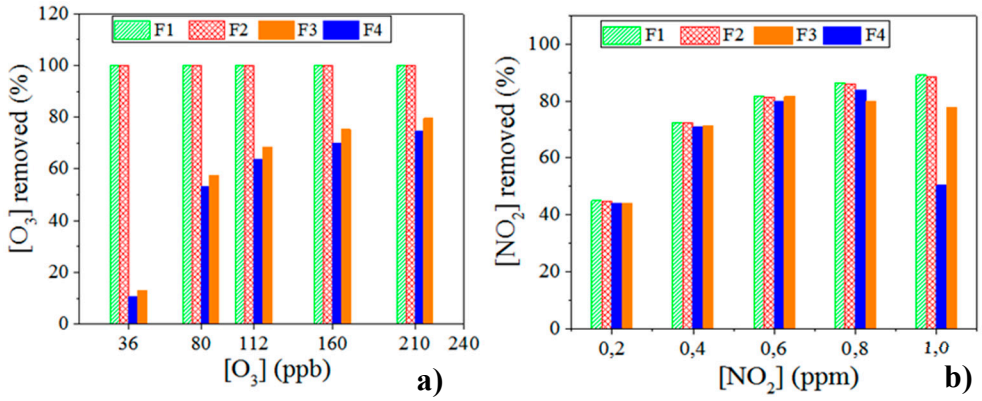

Figure 2. Amount of gas removed by the four filters F1, F2, F3 and F4 as a function of initial concentration: (**a**) under O_3 and (**b**) under NO_2.

This work will also be enriched with future experiments combining humidity, gas mixture and filter. These ongoing experiments will allow to define the best conditions of use of filters coupled to the microsensors.

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Conflicts of Interest: The authors declare no conflict of interest.

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