



HAL
open science

Selective Detection of NO₂ with Specific Filters for O₃ Trapping

Mehdi Othman, Christophe Théron, Marc Bendahan, Charles Rivron, Sandrine Bernardini, Guillaume Le Chevallier, Ludovic Caillat, Khalifa Aguir, Thu-Hoa Tran-Thi

► **To cite this version:**

Mehdi Othman, Christophe Théron, Marc Bendahan, Charles Rivron, Sandrine Bernardini, et al.. Selective Detection of NO₂ with Specific Filters for O₃ Trapping. Proceedings, 2017, 1, pp.405. 10.3390/proceedings1040405 . cea-01578915

HAL Id: cea-01578915

<https://hal-cea.archives-ouvertes.fr/cea-01578915>

Submitted on 30 Aug 2017

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Selective Detection of NO₂ with Specific Filters for O₃ Trapping †

Mehdi Othman ¹, Christophe Théron ², Marc Bendahan ¹, Charles Rivron ², Sandrine Bernardini ¹, Guillaume Le Chevallier ², Ludovic Caillat ², Khalifa Aguir ^{1,*} and Thu-Hoa Tran-Thi ²

¹ Aix Marseille Univ, Université de Toulon, CNRS, IM2NP, 13397 Marseille, France;

mehdi.othman@im2np.fr (M.O.); marc.bendahan@im2np.fr (M.B.); sandrine.bernardini@im2np.fr (S.B.)

² NIMBE, CEA, CNRS, Université Paris-Saclay, CEA-Saclay, 91191 Gif sur Yvette Cedex, France;

christophe.theron@cea.fr (C.T.); charles.rivron@cea.fr (C.R.); guillaume.le-chevallier@cea.fr (G.L.C.);

ludovic.caillat@cea.fr (L.C.); thu-hoa.tran-thi@cea.fr (T.-H.T.-T.)

* Correspondence: khalifa.aguir@im2np.fr; Tel.: +33-(0)491-288-972

† Presented at the EuroSensors 2017 Conference, Paris, France, 3–6 September 2017.

Published: 28 August 2017

Abstract: The present study evaluates the ozone (O₃) and nitrogen dioxide (NO₂) 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 O₃ trapping. The gas removal effectiveness of the filters was assessed through measurements of O₃ concentrations in the air upstream and downstream of the filters. Depending on the filter nature, O₃ can be totally trapped while NO₂ 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 (O₃) is an air pollutant produced by photochemical reactions and chemical reactions between oxides of nitrogen (NO_x) and volatile organic compounds (VOC). High outdoor O₃ concentrations have been linked to asthma exacerbation, respiratory symptoms, heart attacks and premature death. In addition to the direct health risks, O₃ can also chemically react with various indoor pollutants [1,2] to produce more toxic volatile compounds. Since O₃ is the main interfering pollutant for NO₂ monitoring in the context of air quality control, various filters (nanocarbon, indigo thin film or MnO₂) were proposed and were found to efficiently trap O₃ without trapping NO₂ [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 O₃ and weakly reactive with NO₂ 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 O₃. 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 synthesized filters will be tested in order to quantify their ability of O₃ trapping under various conditions. The second part is dedicated to the selection of filters to be used for NO₂ detection in O₃ environment. Various tests have been performed to check the total O₃ trapping by the filters with sensor and NO₂ detection with WO₃ based gas sensor using various O₃ 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 (CITMOS). TMOS or a mixture of TMOS with either PhTEOS or CITMOS 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, $70 \text{ g}\cdot\text{L}^{-1}$, 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·L ⁻¹	Drying Time Days	Sads m ² ·g ⁻¹	V3 cm ³ ·g ⁻¹
F1	TMOS/PhTEOS/MeOH/H ₂ O 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/CITMOS/MeOH/H ₂ O 0.8/0.2/4/4	0.0271	38	8 ± 2 100% (25–70 Å)	0.01
F3	TMOS/CITMOS/MeOH/H ₂ O 0.5/0.5/4/4	0.0263	32	Non porous	-
F4	TMOS/CITMOS/MeOH/H ₂ O 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·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 O₃ and NO₂

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 WO₃ sensitive layer (50 nm thick) produced by reactive R.F (13.56 MHz) magnetron sputtering and can detect both O₃ and NO₂. 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 NO₂ and O₃ is studied under several pollutant concentrations, from 200 ppb to 1000 ppb for NO₂ and from 36 ppb to 210 ppb for O₃. 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.

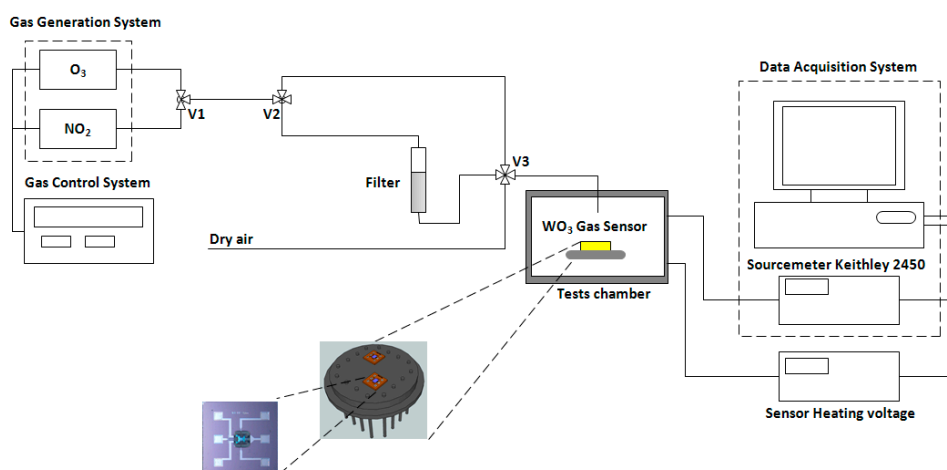


Figure 1. Experimental setup for gas sensors and filters tests.

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.

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

3. Results and Discussion

In order to evaluate the efficiency of O₃ and NO₂ trapping, different measurements were carried out for each filter filled with 1.79 g of filtering material and placed up-stream of the WO₃-based sensor. F1 and F2 filters were found to remove completely O₃ but not NO₂ as shown in Table 2. In contrast, F3 and F4 which display no porosity only partially remove O₃ and NO₂.

Table 2. Filter trapping performance under O₃ and NO₂.

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 O₃ is further tested with reduced amounts of filtering material (0.2 g). As shown in Figure 2a, F1 and F2 can still completely eliminate O₃ 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 O₃ removal is increased with increasing O₃ concentration. In other terms, this means that the O₃ amount passing through the filter decreases as the up-stream concentration O₃ increases.

On the other hand, and unlike the O₃ case, all the filters remove partially NO₂ as illustrated in Figure 2b and the NO₂ removal appears to be dependent on the up-stream NO₂ concentration.

These preliminary results clearly indicate that F1 and F2 can efficiently trap O₃ and could be used to measure NO₂ in gas mixtures containing both pollutants. Further experiments will be needed to find out the range of NO₂ concentration over which F1 and F2 could be used up-stream of the sensor for the measurements of NO₂ in air.

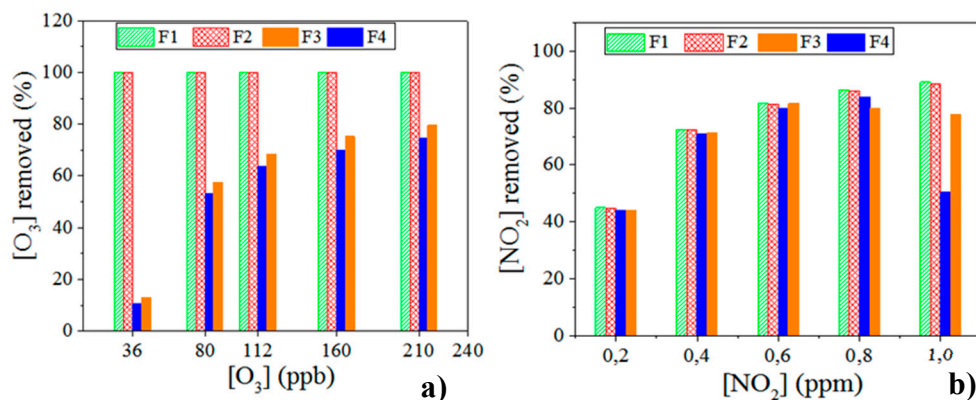


Figure 2. Amount of gas removed by the four filters F1, F2, F3 and F4 as a function of initial concentration: (a) under O₃ and (b) under NO₂.

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.

Acknowledgments: This research is supported by bpi-France in the framework of the SMARTY Project (Smart AiR qualiTY). The authors gratefully acknowledge A. Combes and T. Fiorido, from the IM2NP, for their technical assistance.

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

References

1. Weschler, C.J. Ozone's impact on public health: Contributions from indoor exposures to ozone and products of ozone-initiated chemistry. *Environ. Health Perspect.* **2006**, *114*, 1489–1496.
2. Apte, M.G.; Buchanan, I.S.; Mendell, M.J. Outdoor ozone and building-related symptoms in the base study. *Indoor Air* **2008**, *18*, 156–170.
3. Brunet, J.; Dubois, M.; Pauly, A.; Spinelle, L.; Ndiaye, A.; Guérin, K.; Varenne, C.; Lauron, B. An innovative gas sensor system designed from a sensitive organic semiconductor downstream a nanocarbonaceous chemical filter for the selective detection of NO₂ in an environmental context. Part I: Development of a nanocarbon filter for the removal of ozone. *Sens. Actuator B Chem.* **2012**, *173*, 659–667.
4. Viricelle, J.-P.; Pauly, A.; Mazet, L.; Brunet, J.; Bouvet, M.; varenne, C.; Pijolat, C. Selectivity improvement of semi-conducting gas sensors by selective filter for atmospheric pollutants detection. *Mater. Sci. Eng. C Elsevier* **2006**, *26*, 186–195.
5. Aguir, K.; Bendahan, M.; Laithier, V. Heated Sensitive Layer Gas Sensor. U.S. Patent, 20160238548 A1, 18 August 2016.



© 2017 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).