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The use of the substituted imidazoline radical as a receptor for sulphur dioxide gas sensor

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Abstract

Computer simulation of different structures of adsorption complexes formed by gas adsorption on organic layers with various functional groups was carried out. On the basis of simulation results, we chose 2-(4′-dimethylaminophenyl)-4,4,5,5-tetramethylimidazoline-3-oxide-1-oxyl as a substance possessing high selectivity toward SO_2. Simulation results were confirmed experimentally in the studies of adsorption by means of ellipsometry and quartz microbalance.

Keywords: Selective adsorption; Gas sensor; Modeling of adsorption complex

1. Introduction

Development of solid-phase chemical gas sensors involves selection of a sensitive layer with selective adsorption centres. Analysis of the functioning mechanism of olfactory organs in living organisms suggests that specificity and sensitivity of receptor centres can be determined by the guest-to-host or key–lock type interactions. The presence of a functional group able to play the role of a host or a key is necessary to detect a gaseous component or dispersed phase. The use of organic molecules as receptors provides essential advantages in selectivity, and the goal is to build these groups into a solid-phase matrix. Several methods can be used to build functional groups into films: sol–gel technology, modification of silica gels from liquid or gas phases, Langmuir–Blodgett film deposition (LB), or preparation of clustered films by means of evaporation in vacuum.

In order to register SO_2, it was proposed in [1] to use substituted amines as receptors. Sulphur dioxide is a weak Lewis acid and thus it forms complex compounds of donor–acceptor type with amines. On the basis of IR spectroscopic studies carried out previously, the formation of adsorption complex (AC) was demonstrated [2,3]; it was established that the adsorption power of amines increases with an increase in the number of methyl groups at the amine nitrogen atom [1]. Modeling performed by us also indicates that adsorption power of amines increases with an increase in the number of methyl groups and with their substitution by ethyl groups; however, the same calculations indicate that these layers also absorb water, which has been confirmed experimentally. To solve this problem, the working temperature of the sensor can be elevated to reduce the adsorption ability towards water. However, this does not provide a complete solution of the problem, because the adsorption power toward SO_2 also decreases. The search for a receptor for SO_2 is still an urgent task. For instance, a sensor based on an organic polymer with different amino groups was proposed in [4].

Recently, complicated organic molecules have become a subject of extensive investigation for use as receptors. Examples of the use of phthalocyanines and porphyrins as sensors for such gases as Cl_2, NO_2, and NO are described in [5–9]. We made an attempt to search for selective receptors by means of modeling the AC with various environmentally significant gases. Semi-empirical MNDO procedure was applied for simulation. Some simulation results were checked in experimental studies of adsorption.

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2. Modeling and experiment

2.1. Search for receptor compounds

Organic compounds with various functional groups were considered as receptor centres. These compounds included secondary and tertiary amines, amides, esters, carboxylic acids, hydrocarbon fragments with double or triple bonds in different positions, nitroxide radicals. The compounds were synthesized to be deposited using Langmuir–Blodgett procedure. The formulas of some of the considered compounds are shown in Table 1.

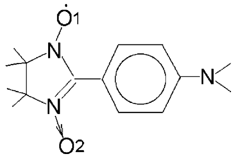
The organic compounds were tested for adsorption of such gases as NO_2, NO, CO_2, CO, H_2S, H_2O, NH_3, Cl_2. Some most notable preliminary results concerning adsorption of the abovementioned gases are briefly outlined below.

Hydrogen sulphide (H_2S): as the results of preliminary simulation suggest, the most suitable sorbing compound is (6); a compact AC is formed in this case; the S–N distance is 3.005 Å; adsorption is reversible, since the energy of AC formation is only about 6 kcal/mol. Attention should be paid to the fact that compound (6) readily adsorbs only hydrogen sulphide. This compound was deposited onto silicon plates; some preliminary experiments on H_2S adsorption were carried out by means of ellipsometry. It was confirmed that (6) adsorbs H_2S specifically, while compound (5) does not possess this ability.

Nitrogen dioxide (NO_2): according to calculation results, several compounds adsorb NO_2 (2, 4, 5, 7), but they also adsorb SO_2.

As a rule, the presence of C=O group results in the formation of stable AC with H_2O, which strongly decreases selectivity of the deposited layers. For instance, compound (7) forms a stable AC with SO_2; the energy of its formation is about 11 kcal/mol; the AC is formed with the amine group. The presence of C=O group does not have a significant effect on the formation of AC with SO_2; at the same time, C=O group forms an AC with water molecule; the energy of formation is about 12 kcal/mol. As a rule, adsorption of water causes substantial changes in the dipole moment, which may interfere with the detection of a useful signal of SO_2 adsorption.

Basing on preliminary simulation performed by us, we chose compound (8), 2-(4′-dimethylaminophenyl)-4,4,5,5-tetramethylimidazoline-3-oxide-1-oxyl (DAPTIOO), which promises unique adsorption properties. The results of calculation indicate that this compound possesses high selectivity to SO_2. The structural formula of this compound is shown here, where oxygen atoms are numbered for clarity.



2.2. Modeling of the adsorption complex

Modeling (simulation) of the AC of SO_2 with DAPTIOO was carried out by minimizing energy with the help of semi-empirical MM2, MNDO procedures [10,11]. Stability criteria for the AC were: (i) AC formation energy, (ii) bond length in the AC. Dipole moment can also be used as a parameter to characterize the properties of the resulting AC.

2.3. Experimental studies

Adsorption was also investigated experimentally in order to verify simulation results. The amount of adsorbed gas was measured using a fast-operation automatic LEF-701 ellipsometer. The working wavelength of the ellipsometer was $\lambda = 632.8$ nm, and the angle of the ray falling onto the sample was $\phi_0 = 70°$. A quartz crystal microbalance (QCM) was also used for this purpose. Measurements were carried out with the ellipsometric set-up equipped with a special chamber to admit active gases. Carrier gas was specially dried nitrogen. All the measurements were carried out at room temperature. In order to determine initial thickness (d) and refractive index (n) of the layers, we made multi-angle measurements (five angles) with a hand-operated ellipsometer LEF-3A with the working wavelength of $\lambda = 632.8$ nm. For QCM, quartz plates (AT-cut) for the frequency of 10 MHz were used. The sensitivity of the quartz microbalance was not worse than 0.3×10^{-8} g/Hz, according to our estimation.

The IR transmission spectra of the films were recorded with a Fourier transform Bruker IFS-113V spectrometer within the wavenumber range 400–4000 cm^{-1} with a resolution of 1 cm^{-1}.

The layers were deposited on substrates using LB method and vacuum sputtering. Sputtering was performed at a pressure of $\sim 2 \times 10^{-5}$ Torr, and the evaporation temperature was a little above the melting point of the compound at about 160 °C. The

Table 1
Calculated parameters of the AC of SO_2 with organic molecules

Organic molecule	ΔE (kcal/mol)	ΔD (Debye)	Δd (Å)
(1) $(C_2H_5)_2$–N–$CH_2C{\equiv}C(CH_2)_{21}$–$COOCH_3$	5.09	1.574	3.50
(2) $CH_2{=}CH$–CONH–$C_{18}H_{37}$	9.11	1.598	2.82
(3) $CH_3(CH_2)_{11}C{\equiv}CCH_2CONHR_1$	10.29	1.124	2.94
(4) $CH_3(CH_2)_{14}CONHCH_2(C{\equiv}C)_2(CH_2)_8OH$	8.78	3.654	2.97
(5) $CH_3(CH_2)_{16}(C{\equiv}C)_2(CH_2)_8CONHR_2$	10.13	1.558	2.96
(6) $CH_3(CH_2)_{16}(C{\equiv}C)_2(CH_2)_8CONHR_1$	10.16	1.513	2.95
(7) $C_{17}H_{35}(C{\equiv}C)_2(CH_2)_8CONH$–$Ph(Me)_4O^{\bullet}$	10.29	1.124	2.94
(8) DAPTIOO	14.2	0.902	2.29

Note: R_1, pyridyl-1; R_2, pyridyl-3.