A colorimetric CO sensor for fire detection

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Abstract

We report on a colorimetric carbon monoxide (CO) sensor based on a rhodium complex. The sensor relies on changes in the light absorption properties of the chemochromic reagent when exposed to the gas. Its optical properties in solution and in a polymeric matrix were investigated by spectrophotometry. A strong color change from purple to yellow was obtained when exposed to CO. For its implementation in a sensor configuration, the complex embedded in a PVC-based matrix was spin-coated onto a glass waveguide. The sensor was tested in a gas cell and with standardized test fires. It showed a high sensitivity to low concentrations of CO, a fast reaction time and complete reversibility. The device may find applications in the field of fire detection and indoor air quality monitoring.

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1. Introduction

Standard fire detectors rely on the measurement of backscattered light emitted by an LED and reflected on smoke particles. Such devices have a long response time, do not detect non-smoking fires and suffer from false alarms. To circumvent these drawbacks, systems based on gas instead of particle detection would provide faster and more accurate fire detectors since gases are generated before aerosols. Metal-oxide gas sensors have already been investigated for this application [1]. However, they suffer from high power consumption and a lack of selectivity. Here, a colorimetric sensor for CO detection is presented. It is based on the color change of a chemochromic film when exposed to the analyte [2]. In this study, a new rhodium complex for CO detection was synthesized and embedded in a polymeric matrix.

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A sensitivity to CO of -33 mV/ppm was measured and a theoretical limit of detection of 0.84 ppm was computed.

2. Experimental

The sensing function of the rhodium(II) complex 2 is based on its ability to bind different molecules in axial sites, which can cause a color change in the visible region. The ability of dinuclear Rh(II) compounds to form labile adducts by coordinating different donor ligands in these axial positions has been well investigated [3]. Recently, Esteban et al. have described the Rh complex 1 which can be used as a chemosensor for CO [4]. In order to increase the sensitivity and stability, we have synthesized the new complex 2 by substitution of the acetate ligands with trifluoroacetate (Figure 1).

Complex 2 was embedded in a polymeric matrix composed of a polymer and a plasticizer. The combination of polymethyl methacrylate (PMMA), polydimethyl siloxane (PDMS), polyvinyl chloride (PVC), polyvinyl butyral (PVB) or ethyl cellulose as polymer, with dioctyl sebacate (DOS), dioctyl phthalate (DOP), tributyl phosphate (TBP) or 2-nitrophenyloctyl ether (NPOE) as plasticizer were investigated.

The solutions were drop-coated on glass slides to obtain layers thick enough (few tens of μm) for spectrophotometric measurements (Lambda 900 from Perkin Elmer). They allowed defining the wavelength of the maximum variation of light absorption when the complex was exposed to CO and to perform stability tests. For the deposition on a waveguide, a 300 nm thick layer of the colorimetric film was spin-coated onto modified glass slides (Figure 2a and 2b). It acted as a planar optical waveguide in which the light propagates by total internal reflection. An LED was used as light source. The detectors were two photodiodes, one for the actual gas concentration measurement and one as reference. The latter kept the light intensity of the LED constant through an analog feedback loop. The waveguide and the electronic circuit were placed in a gas cell that was used for both laboratory measurements and standardized test fires (TF) (Figure 2c).

3. Results

Spectroscopic measurements (Figure 3) were performed with the dye in solution and in a polymeric matrix. When exposed to CO, a color shift from purple to yellow occurred. The highest stability was
obtained with the Rh complex was embedded in a matrix of PVC and TBP. With the other evaluated polymers and plasticizers, the dye reacted with the matrix components. Two maxima of color variation were observed. The highest variation occurred at a wavelength of 405 nm and a second variation at 582 nm. The latter was selected for building the optical system of the gas cell since the combination of a yellow LED (TLYK1100C, Toshiba, $\lambda_{\text{max}} = 590$ nm) and a photodiode (BPW34, Osram) were more cost-effective than an optical system operating in the blue region of the spectrum. Measurements in the other range would be of interest to define the impact of the wavelength on the characteristics of the sensor.

Figure 4a depicts the results obtained when the sensor was exposed to CO concentrations between 5 and 40 ppm in synthetic air with 30% humidity background. The sensor had a sensitivity to carbon monoxide of -33 mV/ppm. The theoretical limit of detection [2] was determined to be 0.84 ppm, well below typical minimal CO concentrations (about 5 to 10 ppm) in the case of fires. A drift of the signal due to the electronics was observed.

In a second phase, the colorimetric sensor was evaluated with downscaled standardized test fires similar to EN54-7 in a 1 m$^3$ chamber. Exposure to smoldering wood (TF2), smoldering cotton (TF3) and n-heptane (TF5) were performed with the gas cell left opened. To remove the effect of ambient light, flames and smoke aerosols on the sensor signal, a foam filter was used to replace the gas cell cover. The
sensor showed a very good response (Figure 4b). The reaction occurred with a short response time within minutes and full reversibility was obtained.

Fig. 4. (a) Gas response of the colorimetric film when exposed to CO. The gas carrier was synthetic air with a flow of 500 sccm and humidity background of 30%. (b) Colorimetric sensor exposed to different test fires: Smoldering cotton, n-heptane, and smoldering wood. The sensor showed a completely reversibility and a suitable response time for the application. As reference, the CO concentration was monitored with a Binos® 100 from Rosemount Analytical.

4. Conclusion

The synthesis of a new Rh complex for carbon monoxide detection is presented. The complex was embedded in a polymeric matrix made of PVC with TBP as plasticizer. For gas measurements, the colorimetric film was spin-coated onto a planar optical waveguide combined with LED and photodetectors. The sensor exhibited a completely reversible reaction when exposed to CO. A sensitivity of -33 mV/ppm was measured and a theoretical LOD of 0.84 ppm was computed. When exposed to standardized test fires, a fast response of the sensor was observed. The cross-sensitivity still need to be evaluated. The sensor presented here shows a strong potential for CO measurements with possible applications in the field of fire detection and ambient air monitoring in buildings.

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