Sensors and Actuators B 215 (2015) 464–470

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

Effect of Fe doping on the CO gas sensing of functional calixarene molecules measured with quartz crystal microbalance technique

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ARTICLE INFO

Article history:
Received 8 October 2014
Received in revised form 24 February 2015
Accepted 3 April 2015
Available online 15 April 2015

Keywords:
Fe doped calixarene molecules
Quartz crystal microbalance
CO gas sensing

ABSTRACT

This article presents comprehensive studies of carbon monoxide (CO) responses of bare and iron doped six calix[4]arene derivatives substituted with various functional groups based on quartz crystal microbalance (QCM) technique. The functional groups in calixarene molecules were chosen to increase the affinity towards CO. The sensitive films were prepared by using drop casting method on a QCM gold electrode with resonance frequency of 7.995 MHz. The responses of bare and Fe doped calixarene molecules were investigated in details. Our QCM results showed that although both bare and Fe doped calixarene molecules are very sensitive to CO gas and Fe doped calixarene molecules have higher affinity to CO about 27.88 times greater than bare are. Therefore, these results open an approach to create new materials for the gas sensing applications.

1. Introduction

Toxic gas sensors are urgently needed for industrial health and safety, environmental monitoring and process control. Carbon monoxide (CO) is a toxic gas and dangerous for human life due to the fact that it is odourless and colorless, making it undetectable by human sensing mechanism. Therefore, the requirement for cheap, reliable and sensitive CO sensors is the key point for academic and industrial world. The investigation of novel type of materials and sensing techniques are needed for comprehensive research in the field of gas sensor. As calixarenes have nano-size structure, excellent sorption abilities and selectivity, long time stability, technological feasibility, they are promising organic materials for sensor applications [1,2]. In addition, they are macro cyclic molecules that can be easily functionalized from their upper and lower rims [3]. The functional groups at the upper and lower rims determine the selectivity in host–guest interactions and physical properties of calixarene molecules [4,5]. Physical properties of calixarene molecules are strongly dependent on the functional groups attached to lower rim. Furthermore, the calixarene molecules having the apolar cup-shaped cavity can easily interact with the unknown molecules (called guest molecule) at the nanoscale level [6]. These interactions can be called adsorption and desorption processes which are the essential for gas kinetics in sensor applications.

In gas sensor applications, there are several techniques based on the conductivity, optical, frequency shift (Quartz Crystal Microbalance, QCM) and Surface Acoustic Wave [7]. Among these techniques, QCM is the powerful method because of sensitivity to the mass changes in the nanogram level. QCM electrode responds to any variation in the mass change simultaneously, regardless of the species deposited. QCM monitors the change in mass loading by measuring the shift of its resonant frequency [8]. According to well-known Sauerbrey equation, it is stated that the mass change (Δm) on surface of the quartz crystal is proportional to frequency change (Δf), which is given as;

$$\Delta f = -\frac{2f_0^2}{A\sqrt{\mu\rho}}\Delta m = -C \cdot \Delta m$$

where f_0 is the resonant frequency of the fundamental mode of the QCM crystal, A is the area of the gold disk coated onto the crystal,

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http://dx.doi.org/10.1016/j.snb.2015.04.004
0925-4005/

ρ is the density of the crystal, and μ is the shear modulus of quartz [9].

In the literature, various CO gas sensor systems were investigated by using various functional calixarene molecules [10,11]. Doping of a molecule with metal and/or oxides is one of the most effective techniques to improve gas sensing property of sensor systems. Niu et al. showed that using Fe, Co, and Cr as dopants enhanced the gas sensing property of pure ZnO resulting the $ZnFe_2O_4$ had high affinity and good selectivity to Cl_2 [12]. Moreover, typical dopants like Fe, Ti and Sn was also used to investigate different effects on the gas sensing characteristic of doped ZnO by Ning et al. [13]. Furthermore, sensing properties of Fe doped SnO_2 thin films was investigated for CO, ethanol and NH_3 gases [14]. However, no research has been found that detailed analysis of CO sensing properties or adsorption–desorption kinetics of pure and Fe doped calixarene molecules based on QCM techniques. Therefore, the main purpose of our study is to investigate CO sensing properties of thin films of bare and Fe doped calixarene molecules coated QCM electrodes. The change of resonance frequency of QCM was measured and analyzed. The results have revealed that the films of Fe doped calixarene molecules have a strong affinity to CO molecules than pure calixarene films.

2. Experimental

2.1. Materials

A Ez-Melt apparatus in a sealed capillary was performed to find out all melting points of the synthesized compounds. A Varian 400 MHz NMR spectrometer, a PerkinElmer 100 FTIR spectrometer, and an elemental analysis branded with Leco CHNS-932 analyzer were used to determine structure of all synthesized products. The reactions were monitored by using TLC analyses obtained from Merck (DC Alufolien Kieselgel 60 F_{254}). All starting materials and reagents used were of standard analytical grade from Merck or Aldrich and used without further purification.

2.2. Synthesis of functional calixarene derivatives

The calixarene molecules were synthesized according to previous procedure [11,15–19].

2.2.1. Synthesis of 5,11,17,23-tetra-4-(ethylaminomethyl) pyridine-25,26,27,28-tetra-hydroxy calix[4]arene (C2)

Yield: 71.1%, m.p. > 350 °C. ^{1}H NMR ($CDCl_3$): δ = 1.02 (t, 12H, J = 7.2 Hz, CH_3), 2.42 (q, 8H, CH_2), 3.28 (s, 8H, CH_2), 3.44 (brs, 12H, CH_2, $ArCH_2Ar$), 4.21 (d, 4H, J = 13.2 Hz, $ArCH_2Ar$), 6.97 (s, 12H, Ar–H, OH), 7.27 (d, 8H, J = 4.8 Hz, Ar–H), 8.49 (d, 8H, J = 5.6 Hz, Ar–H). Anal. Calcd. For $C_{64}H_{72}N_8O_4$(%): C, 75.56; H, 7.13; N, 11.01. Found (%): C, 75.32; H, 8.02; N, 11.10.

2.2.2. Synthesis of 5,11,17,23-tetra-tert-butyl-25,27-bis(2-nitropyridin-2-ylamino)ethylaminocarbonyl-methoxy)-26,28-dihydroxycalix[4]arene (C3)

Yield: 52%, m.p.; 274–275 °C. FTIR (ATR) cm^{-1}: 3450 (–OH), 3380 (–NH), 1670 (C=O), 1481 (N–O asymmetric stretch), 1291 (N–O symmetric stretch). ^{1}H NMR (400 MHz, DMSO): δ 1.06 (s, 18H, Bu^t), 1.14 (s, 18H, Bu^t), 3.28 (d, 4H, J = 13.2 Hz, $ArCH_2Ar$), 3.35–3.58 (m, HOD shielded, 10H, $–CH_2–$ and Ar–NH), 3.91 (d, 4H, J = 13.2 Hz, $ArCH_2Ar$), 4.47 (s, 4H, OCH_2), 6.99 (s, 4H, ArH), 7.08 (s, 4H, ArH), 7.46 (brs, 2H, OH), 8.11 (brs, 2H, ArH), 8.25 (s, 2H, ArH), 8.79 (brs, 2H, ArH), 8.94 (brs, 2H, NH). ^{13}C NMR (100 MHz, DMSO): δ 31.26 ($–CH_3$, Bu^t), 31.80 ($–CH_3$, Bu^t), 34.04 (Ar–CH_2–Ar), 34.47 (–C, Bu^t), 34.49 (–C, Bu^t), 38.05 (–N–CH_2), 72.40 (ArN–CH_2), 74.83 (O–CH_2), 125.74 (ArC), 125.90 (ArC), 126.29 (ArC), 127.17 (ArC), 127.53 (ArC), 133.16 (ArC), 133.29 (ArC), 134.59 (ArC), 141.99 (ArC), 146.96 (ArC), 147.91 (O–CAr), 150.04 (O–CAr), 168.49 (N–CAr, Pyr), 169.72 (C=O). Anal. Calcd. for $C_{62}H_{76}N_8O_{10}$: C, 68.11; H, 7.01; N, 10.25. Found (%): C, 68.26; H, 6.97; N, 10.32.

2.2.3. Synthesis of 5,11,17,23-tetra-tert-butyl-25,27-dihydrazinamidecarbonylmethoxy-26,28-dihydroxy-calix[4]arene (C4)

Yield: 1.6 g (53.3%); mp: 330–333 °C. FTIR (KBr): 1687 cm^{-1} (N–C=O). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.02 (s, 18H, Bu^t), 1.26 (s, 18H, Bu^t), 2.15 (d, 4H, J = 1.6 Hz, NH_2), 3.42 (d, 4H, J = 13.3 Hz, Ar–CH_2–Ar), 4.11 (d, 4H, J = 13.2 Hz, Ar–CH_2–Ar), 4.63 (s, 4H, $–OCH_2$), 6.92 (s, 4H, ArH), 7.10 (s, 4H, ArH), 7.70 (s, 2H, –OH), 9.61 (brs, 2H, NH).

2.2.4. Synthesis of 5,17-bis[(N-methylglucamine)methyl]-25,26,27,28-tetrahydroxycalix[4]arene (C5)

Yield: 39%; m.p.: >350 °C. ^{1}H NMR (400 MHz DMSO): δ 2.49 (s, 6H, $–CH_3$), 3.16–3.63 (br., 34H, $–CH_2–N–$, –CH–, $–CH_2–$, $ArCH_2Ar$, –OH, Ar–CH_2–N–), 4.23 (d, 4H, J = 19.6 Hz, $ArCH_2Ar$), 6.33–6.86 (br, 10H, ArH). Anal. Calcd. for $C_{44}H_{58}N_2O_{14}$; 62.99, C; 6.97, H; 3.34, N. Found: 63.02, C; 6.88, H; 3.32, N.

2.2.5. 5,11,17,23-Tetra-tert-butyl-25,27-di(benzhydrazidylmethoxy)-26,28-dihydroxy-calix[4]arene (C6)

Yield: 98%; m.p.: (161–164) °C. The IR spectral data of **3** is (KBr disk) cm^{-1}: 1638 (–NC=O). ^{1}H NMR (400 MHz $CDCl_3$): δ 1.18 (s, 18H, Bu^t), 1.22 (s, 18H, Bu^t), 2.38–2.42 (m, 4H, $–CH_2–$), 3.37 (d, 4H, J = 12.8 Hz, Ar–CH_2–Ar), 3.54–3.57 (m, 2H, –NH–), 3.76 (t, 4H, J = 6.8 Hz, $–CH_2–$), 4.18 (t, 4H, J = 4.8 Hz, $–CH_2–$), 4.29 (d, 4H, J = 12.8 Hz, Ar–CH_2–Ar), 7.01 (s, 4H, ArH), 7.06 (s, 4H, ArH), 7.39 (s, 2H, –OH), 7.47 (t, 4H, J = 7.2 Hz, ArH), 7.54 (t, 2H, J = 7.2 Hz, ArH), 7.88 (d, 4H, J = 8.0 Hz, ArH), 9.10 (s, 2H, –NH). Anal. Calcd. For $C_{64}H_{80}N_4O_6$ (%): C, 76.77; H, 8.05; N, 5.60. Found (%); C, 76.94; H, 7.91; N, 5.77.

2.3. Preparation of bare and Fe doped calixarene solutions

Six calixarene molecules having different functional groups were used in this study and their chemical names and molecular structures were also given in Fig. 1. For the sake of simplicity, these different calixarene molecules were named as C1, C2, C3, C4, C5 and C6. The calixarene molecules which contain amine groups were preferred so that the acid–base reaction took place during doping process.

Fe doped calixarene molecules were prepared according to following steps; each 1 mM calixarene solution was ultrasonicated for 1 h so that calixarene molecules were solved completely in chloroform($CHCl_3$) (Sigma–Aldrich). 41 mg of iron nitrate ($Fe(NO_3)_3.9H_2O$) (Merck, Darmstadt, Germany) was also solved in 5 ml of ethanol as a second solution. 1 ml of second solution was then added into the perfectly solved 1 ml of each calixarene solution separately. The prepared solutions were ultrasonicated for 12 h. Finally, the solutions were kept at room temperature for 48 h in air.

2.4. Fabrication of QCM based sensor elements

The preparation of QCM electrodes starts with cleaning procedure. Gold coated QCM electrodes were ultrasonically cleaned in acetone, ethanol and 2-propanol liquids (Sigma–Aldrich) for 15 min, respectively and then dried with high purity N_2 gas. Thereafter, 5 μl of each solution was dropped onto gold surface of QCM electrode via micropipette to form a thin film of each sensing material. Afterwards, the electrodes were kept at 60 °C for one hour.

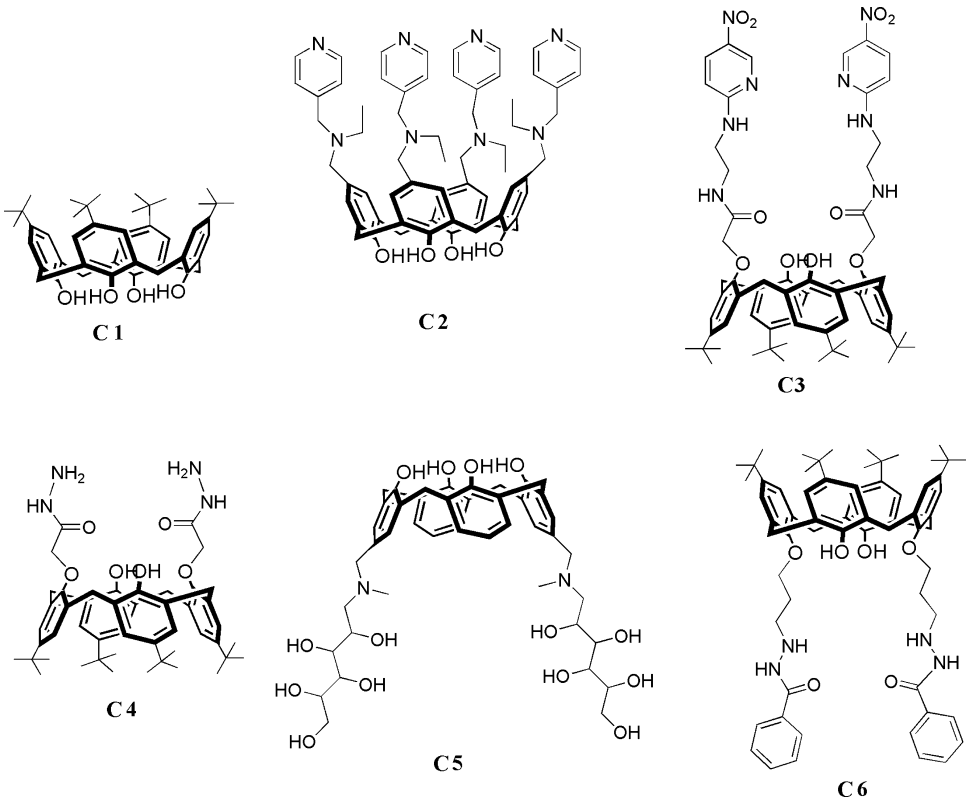

Fig. 1. Chemical names and molecular structures of calixarene molecules.

Finally, the electrodes were kept at room temperature for 48 h for sensor measurements.

2.5. Gas sensor measurements

Adsorption and desorption characteristics of Fe doped and undoped calixarene molecules have been investigated under exposure of CO gas by using QCM technique. 2-channel gas flow system with necessary software and equipment has been developed in our lab. Gas sensor studies of pure and Fe doped calixarene films have been measured by the frequency shift response with flow gas system according to Sauerbrey relation. Fig. 2 illustrates a schematic diagram of the experimental setup. A time-resolved electrochemical quartz crystal microbalance (EQCM) with the model of CHI400A Series from CH Instruments (Austin, USA) has been used to measure the change in the resonance frequency of quartz crystals between gold electrodes via both serial and USB interface connected to a computer. The QCM works with oscillation frequencies between 7.995 MHz and 7.950 MHz. AT-cut quartz crystals with a fundamental frequency of 7.995 MHz have been obtained from International Crystal Manufacturing Co. (ICM). The density (ρ) of the crystal is 2.684 g/cm^3, and the shear modulus (μ) of quartz is 2.947×10^{11} g/cm s^2. Around oscillation frequency of 7.995 MHz, a net change of 1 Hz corresponds to 1.34 ng of gas molecules adsorbed or desorbed onto the crystal surface of an area of 0.196 cm^2. Gas flow into test cell has been supplied by two CO and N_2 calibrated mass flow meters (MKS,179A Mass-Flo®) and RS232 controlled gas flow control unit (MKS precision gas controller, from MKS instruments, Munchen, Germany).

The sensor response for QCM sensors was defined as $\Delta F/\Delta F_o$ where ΔF is the frequency change during CO exposure, ΔF_o is the frequency change of QCM sensors before and after film deposition [20].

3. Results and discussion

In this study, sensitivity properties of six types of Fe doped and undoped calixarenes under exposure of CO molecules (10,000 ppm) have been investigated in detail. Since the functional groups at the upper and lower rims of calixarene molecules determine selectivity in host–guest interactions, C1 has been taken as reference molecule which does not have any functional group compared to others. The functional groups of the other calixarene molecules are slightly different from each other. Since these functional groups are polar, it is expected that they interact with active gas due to unequal charge distribution. On the other hand, conformation of calixarenes is one of the most important factors that affect the dipole moments of calixarene molecules [21,22]. As can be seen from Table 1 and Fig. 3, functionalization of calixarene molecules with different functional group has changed both the dipole moments and three dimensional structures of calixarene molecules. Three dimensional structures and dipole moments of calixarene molecules have been calculated by Density Functional Theory (DFT). All the simulations were performed by using Gaussians09 software. The variations in dipole moments may stem from different functional groups that have different electronegativity and electropositivity. These variations in geometry of calixarenes affected experimental results, as well.

Table 1
Dipole moments of calixarene molecules.

Molecule	Dipole moment components (Debye)			Total dipole moment (Debye)
	μ_x	μ_y	μ_z	μ_{total}
C1	1.44	6.50	1.03	6.74
C2	0.29	−1.45	−0.45	1.55
C3	−3.11	0.84	3.76	4.94
C4	0.63	−7.79	−1.57	7.97
C6	−2.26	−1.15	−0.23	2.55

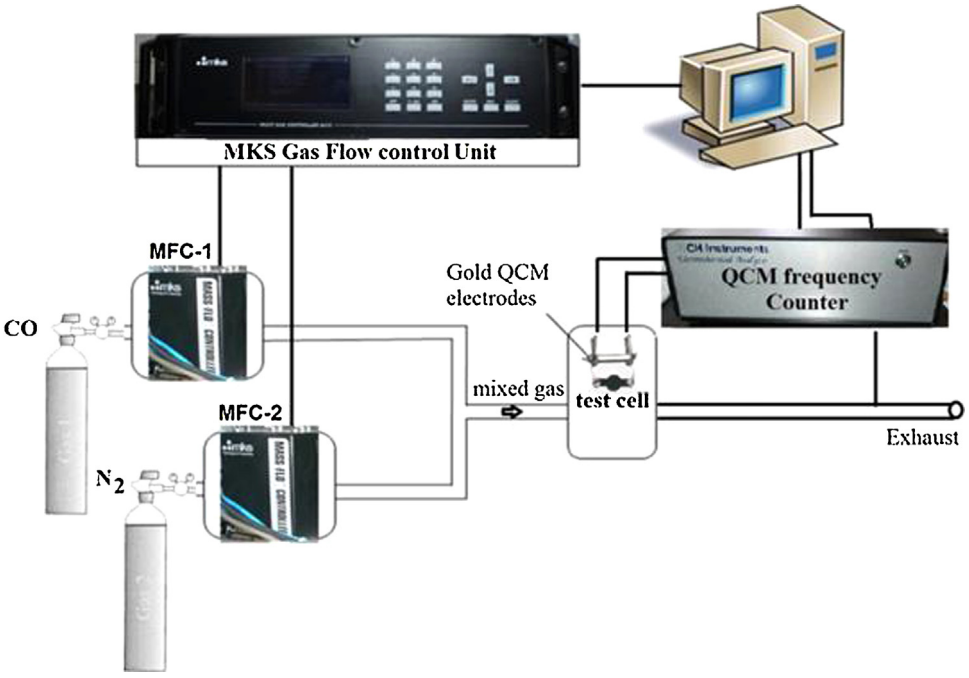

Fig. 2. The experimental setup used to measure the adsorption and desorption kinetics of Fe doped and undoped calixarene films via QCM electrodes.

Fig. 4(a) compares CO responses of bare calixarene film coated QCM electrodes during adsorption and desorption process. Similarly, the results obtained from QCM electrodes coated with iron doped calixarene molecules are presented in Fig. 4(b). Moreover, these on/off response profile of the sensors for 2 cycle's measurement have been given to observe the repeatability of QCM sensors against CO gas. In order to obtain this data, CO and N_2 (500 sccm) were sent consequently with 200 s periods for desorption and 100 s periods for adsorption to observe maximum adsorption and desorption behaviors, respectively. In addition, maximum responses of each molecule to CO are given in Table 2, sorted from largest to smallest.

As can be seen in Table 2, C2, functionalized with pyridine groups, shows highest response to CO molecules compared to other calixarene molecules. Such a high sensitivity may be due to dipole-dipole interaction between CO and nitrogen atom in the pyridine groups. Furthermore, C6 seems to have more suitable three-dimensional structure which means more active sites for CO molecules to be adsorbed. In addition, the response of C5 to CO is less than others. If we look at the molecular structure of C5, it is functionalized with hydroxyl groups and methyl glucamine groups which may give rise to steric effect and do not let CO molecules to get into the active sites of C5. The same effect can also be seen for C1 because of hydroxyl groups from lower rims which causes to hydrogen bond between them. In addition, functional groups, in general, have led to an increase in the CO response of each calixarene compared to reference molecule.

As to QCM results of iron doped calixarene molecules, it is seen that there has been a remarkable increase in the response of each iron doped calixarene to CO up to 200 times compared to bare calixarene molecules. The maximum response of C5 to CO is 0.12; however, it becomes 27.88 when doped with iron. Furthermore, it can be inferred from the results that if the molecular structure of calixarene is suitable to interact with iron molecules, the response of the related molecule to CO increases. More clearly, the more iron exist in molecule, the more sensitive it will be. For example, C2 seems to have three baskets resulting in more sites for iron molecule which increases the affinity of C2_Fe to CO. On the other hand, C4 seems to have only one basket which causes to less amount of iron molecule. Hence, the response of C4_Fe is relatively small compared to other Fe doped calixarenes. The other factor is that Fe^{+3} has binding affinity to OH^-, carbonyl and amino groups [23–25]. The existence of these functional groups may decrease the binding affinity to CO. This interaction may decrease the CO binding capacity of Fe^{+3}. For example, C3_Fe has shown less affinity to

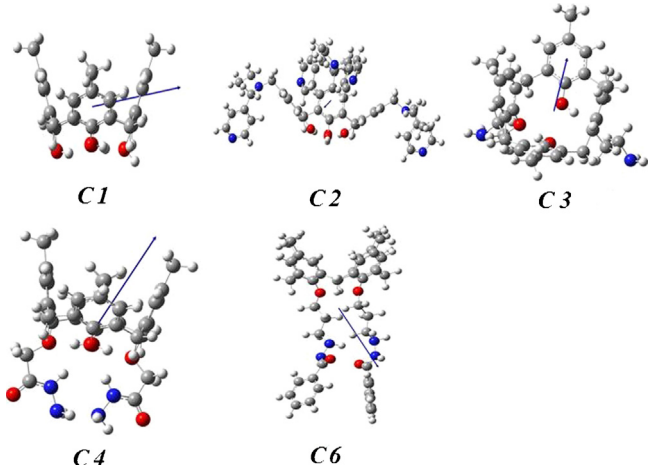

Fig. 3. Three dimensional structures of calixarene molecules.

Table 2
Maximum responses of bare and iron doped calixarenes.

Molecule	CO response	
	Bare	Iron doped
C2	5.16	43.38
C3	0.93	6.57
C4	0.69	12.16
C6	0.66	38.83
C1	0.35 (ref)	(ref)
C5	0.12	27.88

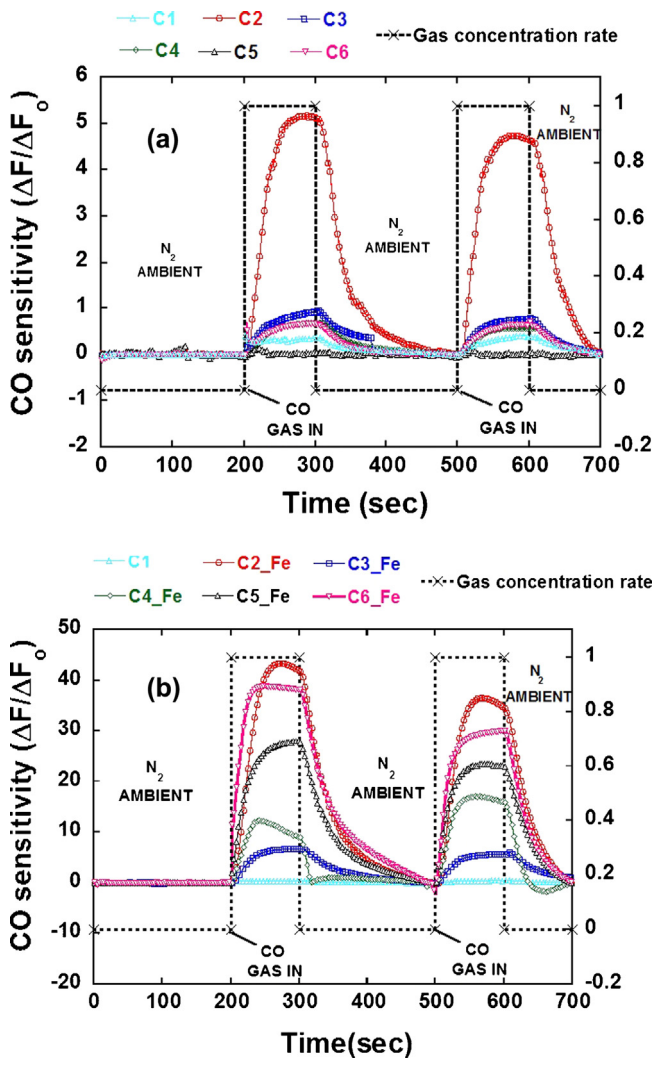

Fig. 4. CO responses for adsorption and desorption process of (a) Bare calixarene molecules, (b) iron doped calixarenes.

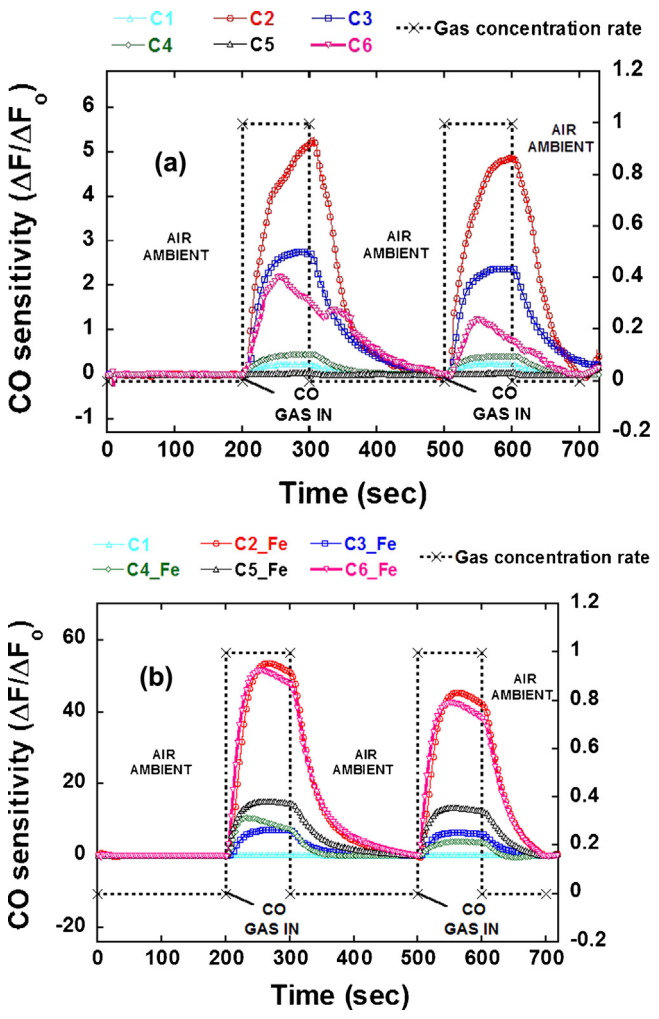

Fig. 5. CO responses in air environment for (a) bare calixarene molecules, (b) iron doped calixarenes.

CO compared to others which may be because of the existence of OH and carbonyl groups in the relevant molecule.

In addition to analysis of sensitivities of all molecules to CO in N_2 environment, the CO sensitivities of all of them have been investigated in air environment. The results are illustrated in Fig. 5(a) and (b). Maximum responses of each molecule to CO in air environment are given in Table 3, sorted from largest to smallest. As seen in Table 3, there is no remarkable change in sensitivities of each molecule when the experiments are carried out in air environment. There has been small decrease in the sensitivity for each molecule to CO in air environment. The molecules virtually give same results which may be due to the fact that air includes 20.95% oxygen, 0.93% argon, 0.039% carbon dioxide and small amounts of other gases as well as 78% nitrogen. These active gases may have occupied the active sites on the surface of molecules.

Table 3
Maximum responses of bare and iron doped calixarenes in air environment.

Molecule	CO response (air environment)	
	Bare	Iron doped
C2	5.34	53.5
C3	2.74	7.10
C4	0.45	10.4
C6	2.18	51.4
C1	0.24 (ref)	(ref)
C5	0.05	15.1

In order to see whether or not the prepared sensors are repeatable and reproducible, each sensing material have been freshly prepared and retested several times. The standard CO sensor measurements similar to Fig. 4(a) and (b) have been repeated in a different laboratory and virtually same results have been obtained even after a long time. For the sake of simplicity, only the maximum CO responses have been given in Fig. 6.

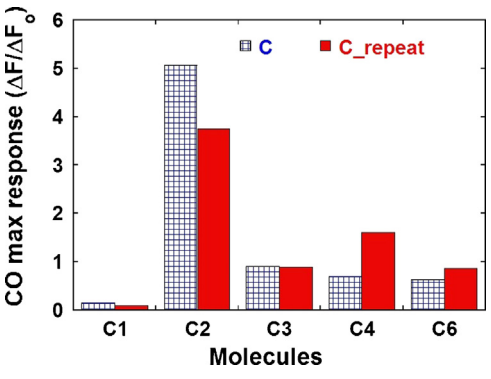

Fig. 6. Repeatability and reproducibility analysis of each calixarene molecule.

Table 4
Detection limits, slopes and linear correlation coefficients (R) of bare and iron doped calixarenes.

Molecule	Slope (Hz/ppm)		Detection limit (ppm)		R	
	Bare	Iron doped	Bare	Iron doped	Bare	Iron doped
C2	0.0030	0.0080	33.3	12.5	0.99	0.99
C3	0.0003	0.0010	333.3	100	0.99	0.85
C4	0.0004	0.0010	250	100	0.98	0.98
C6	0.0003	0.0024	333.3	41.6	0.90	0.94
C1	0.0001 (ref)	(ref)	1000	(ref)	0.87 (ref)	(ref)
C5	0.0001	0.0014	1000	71.4	0.89	0.99

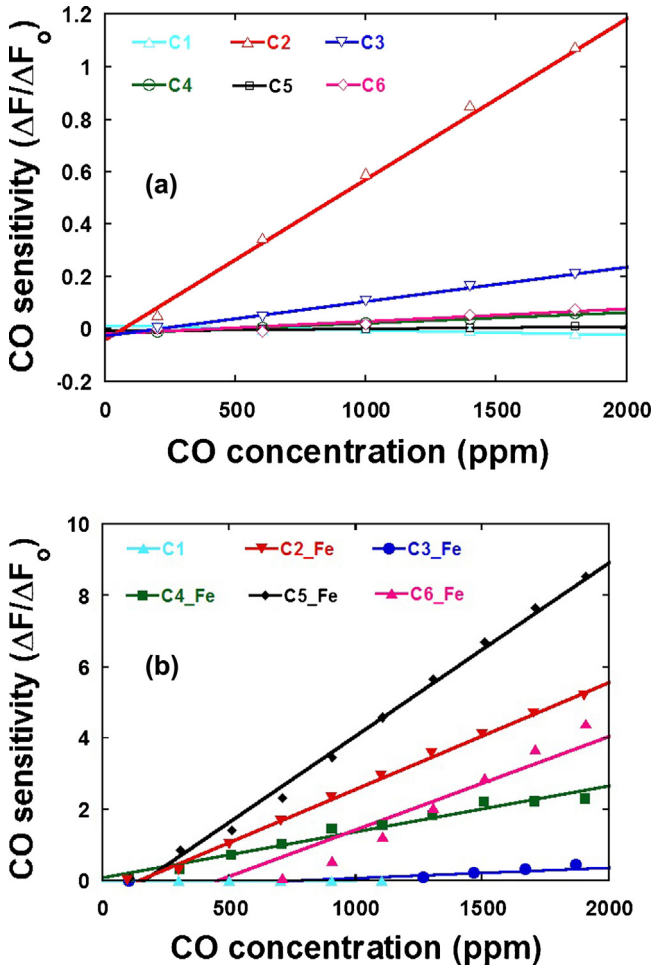

Fig. 7. Linear correlation between response and CO gas concentration for (a) bare calixarene molecules, (b) iron doped calixarenes.

CO concentration dependent gas sensing properties of thin films of iron doped and undoped calixarene molecules have also been reported. The CO level has been increased by 200 ppm steps for equal time intervals of 5 s. Fig. 7(a) and (b) depicts that the interactions of CO molecules with the sensing films are proportional with increasing CO concentration as. It should be noted here that for each calixarene molecule, a linear dependence of QCM response with different slope values to CO concentration has been observed. Here, the detection limit for each QCM system can be calculated by using QCM frequency resolution for CHI400 models which is <0.1 Hz. The slope values, detection limits for 0.1 Hz and linear correlation coefficients (R) have been given in the Table 4 for bare and iron doped calixarene molecules. The detection limits correspond to the sensitivity of sensing films on QCM crystals. This linear behavior is well-known relation described by Sauerbrey equation given above. The mass of adsorbed molecules on calixarene molecules increases with increasing negative frequency shift of calixarene loaded QCM crystal. The sensitivities are much higher for iron doped calixarenes compared to those of undoped calixarenes.

4. Conclusions

Quartz crystal microbalance technique has been used to analyze the CO adsorption and desorption kinetics of bare and iron doped various calixarene films obtained by using drop casting method. The shape of cavity and different functional groups at the lower rims of calixarene molecules have led to variation in the responses of calixarene molecules to CO. It should be emphasized that calixarene molecules with different functional groups have shown high affinity towards CO gas compared to reference molecule. The study has also shown that a remarkable increase in the response to CO has been obtained after doping each calixarene molecule with iron. Furthermore, the responses of bare and iron doped calixarene coated QCM sensors have increased linearly by increasing the concentration of CO gas. Fe doped calixarene materials show a favored kinetic reaction against CO and have potential application for QCM based CO detection at room temperature operation.

Acknowledgements

This research was supported by TUBITAK (Turkish Scientific Association) under project number TBAG 109T240. We are grateful to Dr. Mustafa Can for help with fruitful discussions about the results of organic molecules.

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