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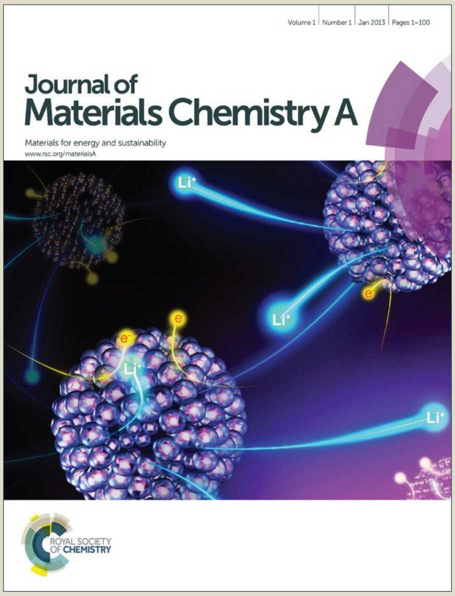

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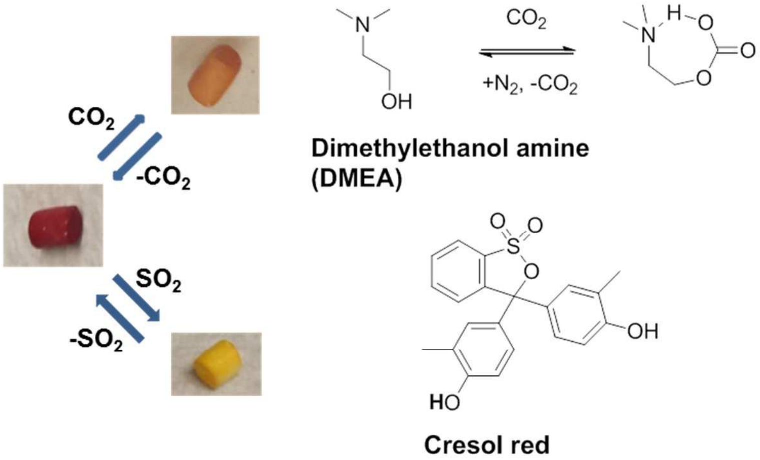

Reusable, solid-supported colorimetric sensors, prepared from tertiary amino alcohols and pH-sensitive dyes, can detect ppm levels of gaseous CO_2 and SO_2.

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ARTICLE

Sensitive Colorimetric Sensors for Visual Detection of Carbon Dioxide and Sulfur Dioxide

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A series of highly efficient, solid-state sensors for direct colorimetric detection of gaseous CO_2 and SO_2 is described. The basic components of the sensors are a CO_2 and SO_2-responsive, tertiary amino alcohol, such as triethanol amine, and a pH-indicator dye *e.g.* cresol red, immobilized on a porous γ-aluminum oxide support. These sensors show distinct visual responses to low levels of CO_2 and SO_2 present in air. A structure-performance relationship was also established for these sensors. To increase the shelf-life, the tertiary amino alcohols were covalently attached to the porous alumina support. These porous alumina-supported tertiary amino alcohols also offer potential for use as adsorbents for acidic gases such as CO_2 and SO_2 with the ability to selectively release these under different conditions, allowing easy separation from a gas stream.

Introduction

The detection of carbon dioxide (CO_2) in confined spaces is of great interest for food, beverage, health, mining, biotechnology, and chemical industries.[1] Many anthropogenic sources of emissions, *e.g.* flue gas and biogas, can contain 15-38% of CO_2.[2] Monitoring the levels of CO_2 present in these gas mixtures allows an indirect quality check for the chemical processes involved and also is essential for effective removal of CO_2 from these gas streams, to curtail green-house emission. To protect the health and safety of the workforces, the concentrations of CO_2 should not exceed 4% (v/v), in a confined area. Upon prolonged exposure, even 2-3% (v/v), CO_2 can affect pH homeostasis, these conditions are believed to cause metabolic syndrome and low plasma-phosphate balance.[3,4]

The most commonly used method for the detection of CO_2 is nondispersive infrared (NDIR) spectroscopy[5,6] for detection of gaseous CO_2 and Severinghaus electrochemical method for aqueous phase detection of CO_2.[7–13] Both of these systems require extensive instrumental set-up and maintenance. Colorimetric or fluorescent CO_2 sensors have also been developed based on a pH indicator and a lypophilic organic base such as a quaternary ammonium salt[14–16] or room temperature ionic liquids.[17] When CO_2 dissolves into water as aqueous bicarbonate the indicator responds to the change in pH of the aqueous layer supported within the sensor matrices. Common limitations of these photo-sensors are the instrumental set-up for digital image readout, long response and regeneration times, limited storage life under ambient conditions. Newer types of CO_2 sensors utilize secondary amines, amidines, guanidines, or *in situ* generated carbenes as liquid phase CO_2 absorbent, in combination with a colorimetric or fluorescent indicator.[18–26] The mode of detection is dependent on the physical changes in the sensor media upon dissolution of CO_2, such as viscosity,[18,19] pH or polarity[24,25]. The common limitations of this approach are multistep synthetic strategy, longer response times, handling and storage of liquid phase sensors, in addition to the formation of stable carbamates which require heated regeneration steps to reuse the sensor. For wide-scale application an ideal CO_2 sensor should be inexpensive, easy to prepare, solid supported, and be able to provide a quantitative, visual read out.

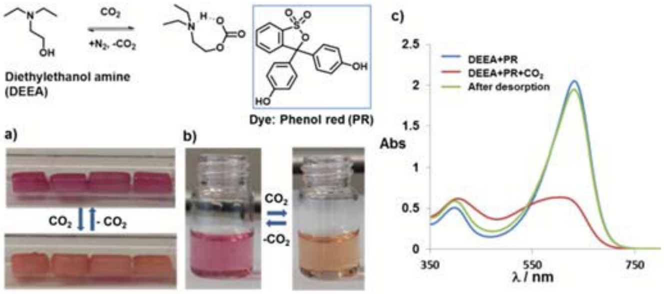


Fig. 1 The observed colorimetric responses of pH sensitive phenol red dye in diethylethanol amine (DEEA) to a flow of pure CO_2 at ambient temperature a) Visual color change observed with alumina-supported DEEA - phenol red system, b) visual color change observed in neat DEEA - phenol red solution, c) changes observed in the UV-visible spectra of neat DEEA - phenol red solution after absorption of pure CO_2 and the subsequent CO_2 desorption by purging with N_2 at ambient temperature.

Herein we report a new series of solid sensor materials for direct colorimetric detection of CO_2 in the gas phase. We also establish a structure-performance relationship to better understand and improve the performance, as well as the storage life of these sensors. The sensors are composed of a pH-indicator dye and a CO_2-responsive tertiary amino alcohol, immobilized on a porous γ-aluminum oxide support. The tertiary amino carbonate formed upon exposure to stream of CO_2, leads to a rapid visible change in the sensor color, as shown in Figure 1. This colorimetric response is completely reversible and is not interfered by moisture, oxygen or <400 ppm CO_2, present in ambient air.

Results and discussion

To demonstrate the activity of these tertiary amino alcohol sensors, the initial experiments were carried out in liquid phase at ambient temperature, in an in situ IR probe. When a steady flow of CO_2 (1 mL/min) was introduced into neat diethylethanol amine (DEEA), two new IR stretches appeared at 1660 cm^{-1} and 1220 cm^{-1}, corresponding to the C=O and C-O vibrations of carbonate, respectively, as shown in Figure 2. When N_2 gas was slowly bubbled into the reaction system at a rate of 1 mL/min, the peaks corresponding to carbonate began to disappear within 5 min.

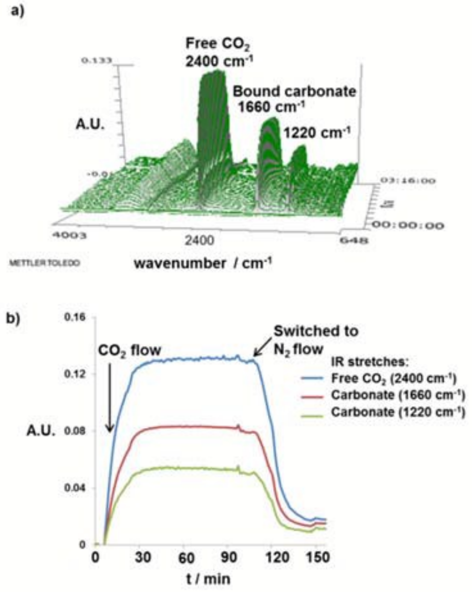
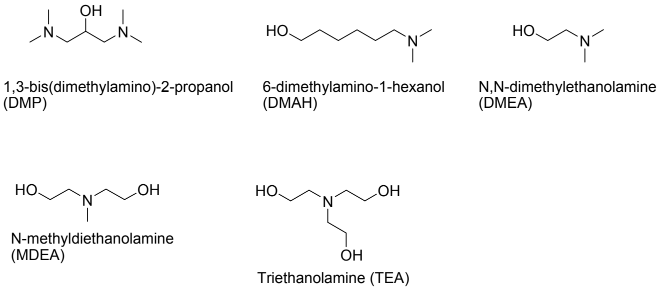


Fig. 2 a) In situ IR spectroscopic monitoring of the reaction between pure CO_2 and neat diethylethanol amine (DEEA). The appearance of new IR stretches at ~ 1660 cm^{-1} and 1220 cm^{-1} (which correspond to the C=O and C-O vibrations, respectively) indicate the formation of carbonate; b) IR stretches due to free CO_2 and bound carbonate form were monitored continuously. Free CO_2 was readily absorbed into solution as carbonate, which was then easily desorbed under a 2mL/min flow of N_2 at ambient temperature.

The ^{13}C NMR spectroscopic analysis of the CO_2 binding, as shown in Figure 3, indicates the formation of carbonate, similar to the report by Heldebrant and coworkers,[27] where the formation of carbonate (158.5 ppm) instead of carbamate (~163 ppm) was observed at 5 bar CO_2 pressure. In order to examine the possibility of bicarbonate formation in the presence of moisture or under humid conditions, we employed a tertiary amine-water system which can capture CO_2 in the form of bicarbonate. Using N,N-diisopropylethylamine, in the presence of 20 μL D_2O, we observe the formation of bicarbonate at 160.3 ppm, (Figs. S2 versus S3). Upon the addition of 20 μL D_2O, the tertiary amino alcohol MDEA also captures CO_2 predominantly in the form of bicarbonate (~161 ppm) as shown (Figs. S4 versus S5). Clearly, in the absence of added water, the amino alcohols bind CO_2 in the form of alkylcarbonate (~159 ppm).

To investigate the versatility of this approach, we screened a series of commercially available, inexpensive tertiary amino alcohols shown in Scheme 1.



Scheme 1 Tertiary amino alcohols screened for their application in CO_2 sensor.

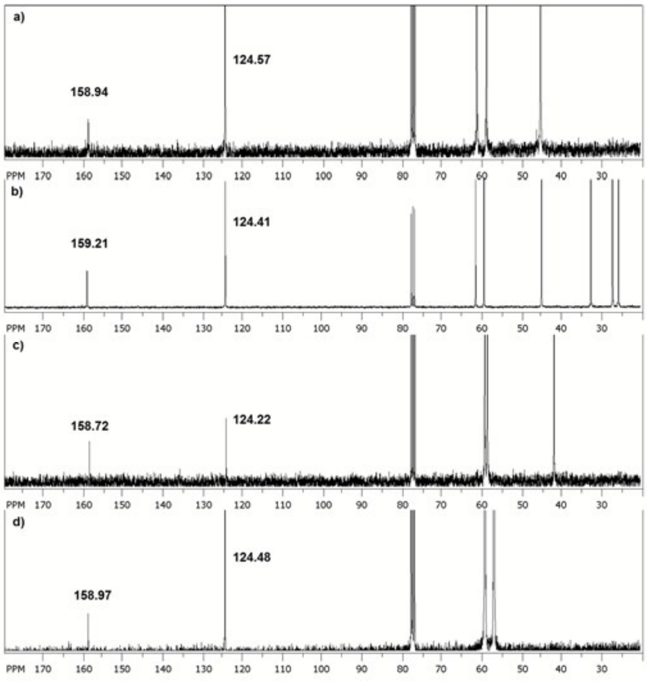


Fig. 3 ^{13}C NMR spectra of $^{13}CO_2$ (free CO_2, 124.4 ppm) binding by a) DMEA, b) DMAH, c) MDEA, and d) TEA. In each case, 70 μL of neat amino alcohol was added to 0.5 mL of $CDCl_3$. The in situ formed carbonate peak was observed ~ 159 ppm.

The liquid sensors were prepared by dissolving 0.1 mg of a pH sensitive dye such as phenol red (PR), bromothymol blue (BTB) or cresol red (CR) in 10 mL of neat tertiary amino alcohol. Except for 1,3-bis(dimethylamino)-2-propanol (DMP), all others show fast colorimetric responses (DMEA, 2 sec; DMHA, 4 sec; MDEA, 11 sec; 40 wt.% TEA in diglyme, 10 sec) to a 1.0 mL/min flow of pure CO_2.

The high viscosity of triethanol amine (TEA) results in limited mass transfer through the solution and the design of an active sensor with TEA required dilution with non-protic solvents such as tetrahydrofuran or diglyme. A 40 wt.% solution of TEA in diglyme, containing bromothymol blue (BTB) indicator, can detect a CO_2 content of 4-6% (v/v), the common amount found in human respiration, as evident from the UV-visible spectrum shown in Figure 4.

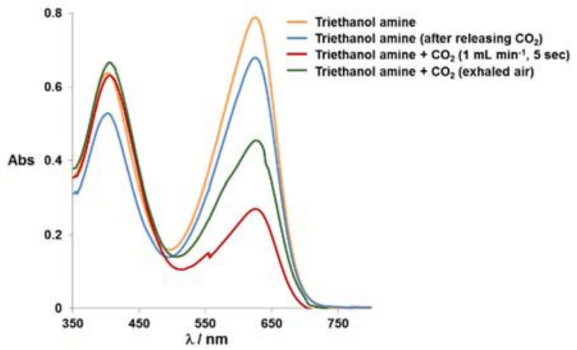


Fig. 4 CO_2 sensing by 40 wt.% triethanol amine (TEA) in diglyme; changes observed in the UV-visible spectra of triethanol amine – bromothymol blue solution upon exposure to the CO_2 in exhaled air or a stream of pure CO_2, followed by the desorption of CO_2.

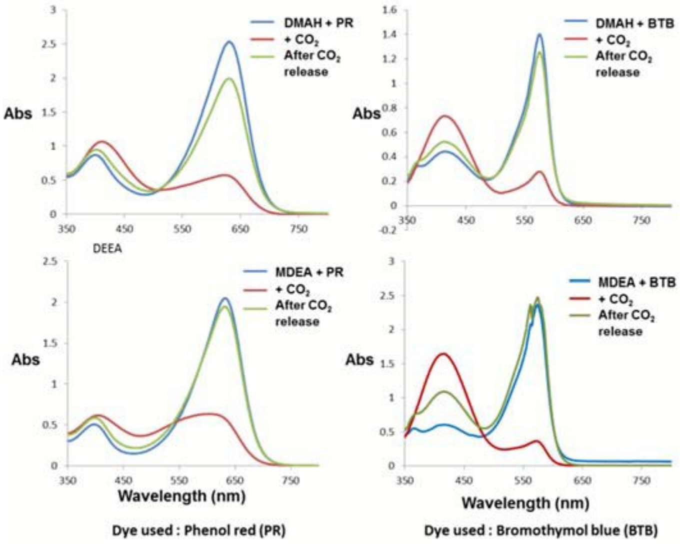


Fig. 5 UV-vis spectral changes observed with a) dimethylamino-1-hexanol (DMHA) and b) N-methyldiethanol amine (MDEA), containing PR or BTB dye, in response to a steady flow of CO_2 (1 mL/min, 30 sec) and after the desorption of CO_2 by passing N_2 at ambient temperature.

Complete regeneration of the liquid sensors is observed within 5 s upon bubbling N_2 through the solution at rate of 2 mL/min at ambient temperature. UV-vis spectral changes observed with this series of amino alcohols in response to CO_2 is shown in Figure 5.

For practical applications, solid-state sensors are preferred over liquids for easier storage and handling. Accordingly, commercial porous γ-alumina pellets were chemically impregnated with the amino alcohols following a method,[28] described in the Experimental Section. The CO_2 binding by these solid phase sensors were investigated by *in situ* IR spectroscopy, as shown in Figure 6.

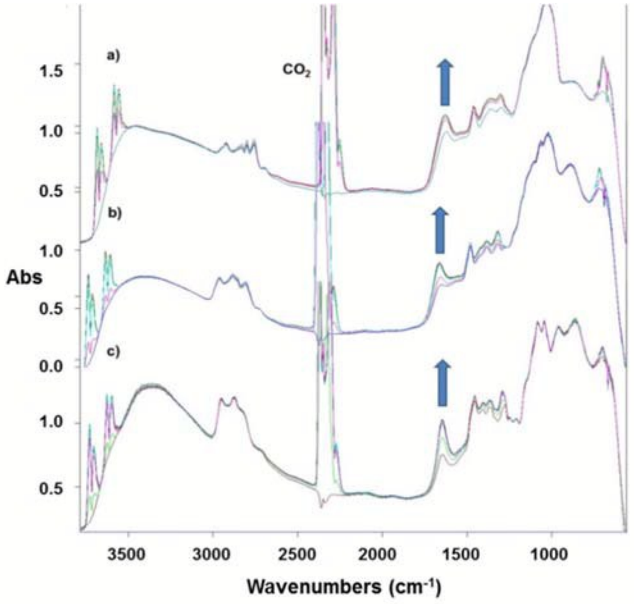
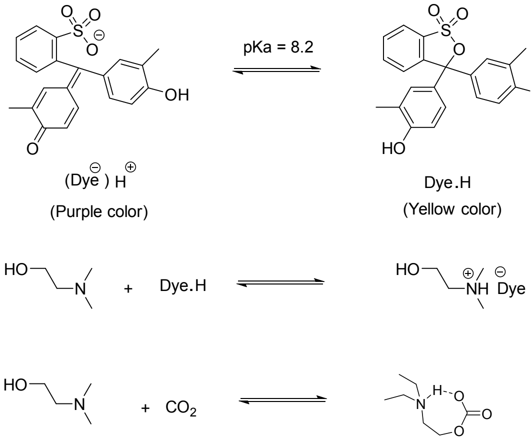


Fig. 6 FT-IR spectroscopic study of CO_2 binding by a) Al_2O_3-DMEA, b) Al_2O_3-MDEA, and c) Al_2O_3-TEA. Arrows indicate the growth of the carbonate stretch (~1660 cm^{-1}) with time. IR spectra were recorded at 60 sec intervals until no further increase in the intensity of the carbonate stretch was observed.

In the presence of a pH-responsive dye, these solid sensors show visual color changes in response to dry CO_2 concentrations as low as 500 ppm, as shown in Figure S1. Similar color changes were also observed when the solid sensors were exposed to 500-2600 ppm CO_2 gas that was pre-saturated with water vapor (Figure 7). In an enclosed environment containing 500-2600 ppm CO_2 in N_2, the observed response times are typically around 10 sec for 500 or 800 ppm CO_2 and 5 sec for >1500 ppm CO_2. The solid sensors readily release CO_2 within 15-20 s when the CO_2 atmosphere is removed and the pellets exposed to air or nitrogen atmosphere. No air or N_2 flow is necessary for regeneration of these solid sensors. These inexpensive solid sensors are ideal candidates for rapid visual estimations of the amount of CO_2 released within enclosed or poorly ventilated work areas. Furthermore, sensors can be easily formulated into simple colorimetric strips or arrays, akin to commonly used pH papers.

Fig. 7 Visual detection and estimation of the amount of prehumidified CO_2 present within an enclosed atmosphere using a) Al_2O_3–dimethylethanolamine-cresol red, b) Al_2O_3–N-methyldiethanol amine-cresol red, and c) Al_2O_3–triethanolamine-cresol red sensors. The visual color changes in response to 500 ppm, 800 ppm, 1600 ppm and 2600 ppm CO_2 in nitrogen are compared with a reference sensor left under ambient air (~ 400 ppm CO_2). In all cases, the CO_2 was pre-saturated with water vapor.

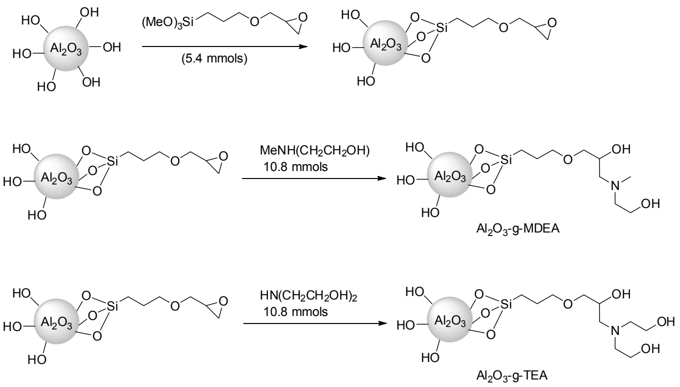
The structural sensitivity of these sensors was also evident from a series of control experiments carried out with bromothymol blue (BTB) or cresol red (CR) indicator using i) N,N'-dimethyl-2-methoxyethylamine ii) triethylamine and an iii) equimolar mixture of triethylamine and ethanol. No color change was observed in these solutions which unambiguously showed that the presence of a tertiary amino alcohol backbone is essential for the formation of the alkylcarbonate moiety.



Scheme 2 The proposed reaction sequence which allows colorimetric response of a pH sensitive dye such as cresol red (CR) to CO_2.

We hypothesize the reaction pathway shown in Scheme 2, based on the protonation-deprotonation equilibrium, previously observed for pH sensitive indicators, such as cresol red.[29–31] Cresol red (CR) undergoes proton exchange with the tertiary amino alcohol to produce the deprotonated anionic dye species: dye$^-$ (purple color). When exposed to CO_2, the amino alcohol forms the zwitterionic ammonium carbonate adduct (unlike primary and secondary amines, tertiary amines do not form carbamates), as observed by Heldebrant and coworkers.[27] This prevents the deprotonation of the dye by the amino alcohol, and the yellow color corresponding to Dye.H is observed.

We also monitored the storage life of the solid sensor pellets. The physisorbed alumina-supported dye-MDEA and TEA systems retained activity for over one month, upon storage in dark, under ambient conditions in air or N_2 atmosphere. The DMEA based sensors showed slow evaporation of DMEA which has the lowest boiling point (133°C) among the current series of amino alcohols. To further extend the shelf-life of the sensors, we followed a covalent grafting approach,[32] as described in Scheme 3. Dry γ-alumina support was allowed to react with (3-glycidyloxypropyl)trimethoxysilane to covalently attach the silyl coupling agent on alumina via hydrolysis of the Si-OMe bonds by the surface hydroxyl groups present on the alumina support. Subsequent ring opening of the pendant epoxide group by an appropriate amine can provide access to the entire series of covalently bound tertiary amino alcohols with one or more - CH_2CH_2OH groups on the nitrogen. The surface grafting reactions carried out with N-methylethanolamine and diethanolamine to obtain the surface bound amino alcohols Al_2O_3-*g*-MDEA and Al_2O_3-*g*-TEA, respectively, were confirmed by FT-IR spectroscopy and the weight loading of the amino alcohol was determined by thermogravimetry coupled with a mass spectroscopic detector. The surface grafted pellets were then soaked in a 10 mM dye solution in tetrahydrofuran to obtain the colorimetric sensors. The solid sensors prepared following the covalent-grafting technique show similar performances to the sensors prepared by chemical impregnation method but retain activity even after an extended shelf storage life of over 3 months.



Scheme 3 Synthetic route for the covalent tethering of tertiary amino alcohols on the surface of alumina using (3-glycidyloxypropyl) trimethoxysilane. The silyl coupling was followed by ring opening of the glycidyl group with secondary amine nucleophiles.

The amino alcohol sensors can also respond to as low as 1,000 ppm and higher levels of SO_2. Figure 8 shows the colorimetric response of these sensors to 0.2% (v/v) SO_2, the second major component, after CO_2 in industrial emissions or flue gas. In contrast to the carbonate derivatives, the SO_2

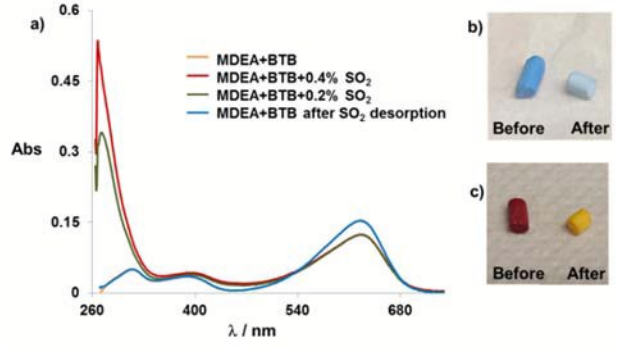


Fig. 8 Detection of trace amounts of SO_2 present in N_2 atmosphere. a) UV-vis spectral changes observed in N-methyldiethanol amine (MDEA)-bromothymol blue solution upon exposure to SO_2 and after its desorption (note that the first and the last curves virtually overlap, suggesting near quantitative desorption of SO_2); b) visual response of an Al_2O_3-MDEA-BTB sensor to a gas mixture containing 0.2 % SO_2 in N_2, c) visual response of an Al_2O_3-DMEA-CR to a gas mixture containing 0.2 % SO_2 in N_2.

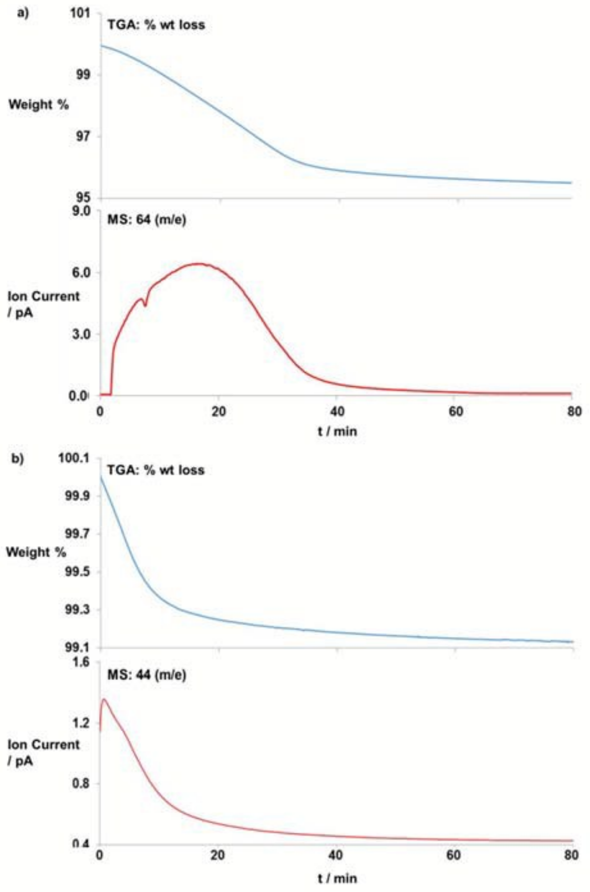


Fig. 9 The desorption of CO_2 and SO_2 from Al_2O_3- N-methyldiethanol amine (MDEA) investigated using thermogravimetric analysis coupled with mass spectroscopy. a) complete desorption of SO_2 (m/e = 64) at 120°C and b) complete desorption of CO_2 (m/e = 44) at 40°C, under 30 mL/min flow of He.

adducts are stable under ambient conditions and can be stored for a period of several days in closed container, preferably under nitrogen, as monitored by FT-IR spectroscopy. To regenerate these sensors, the adsorbed SO_2 can be quantitatively removed by heating at 70°C, under 0.4 torr vacuum for 30 min, or by heating at 120°C for 40 min, under atmospheric pressure. Figure 9 shows the desorption profiles of SO_2 and CO_2 from Al_2O_3-MDEA as monitored by using a TGA analyzer coupled with mass spectroscopic detector. These results suggest that Al_2O_3- MDEA and other alumina supported amino alcohols can sense and adsorb both SO_2 and CO_2, but allow the selective release of these two gases under widely different conditions. The ^{1}H and ^{13}CNMR spectra of MDEA in DMSO-d_6 before and after the reaction with SO_2 are shown in Figs. S7 and S8.

Conclusion

In conclusion, we have fabricated a series of reusable, inexpensive CO_2 and SO_2-responsive solid-state sensors from commercially available tertiary amino alcohols. These sensors are capable of showing distinct visual responses, to ppm levels of CO_2 and SO_2 present in N_2. The presence of water vapor does not interfere with the detection of CO_2. The method allows a qualitative visual estimation of these gases present in the atmosphere, without complex instrumental setup. The sensors are likely to find applications in closed spaces, such as enclosed shipping containers, railroad cars, trailers, submarines, and brewery, where other potentially interfering acidic gases are absent. The porous alumina-supported tertiary amino alcohols also offer potential use as adsorbents for CO_2 and SO_2 with the ability to selectively release these under different conditions, allowing easy separation from a gas stream.

Experimental

Materials

Diethylethanol amine (DEEA), dimethylethanol amine (DMEA), 6-dimethylamino-1-hexanol (DMHA), N-methyldiethanol amine (MDEA), triethanol amine (TEA), 1,3-bis(dimethylamino)-2-propanol (DMP), N-methylethanol amine, N,N-diisopropylethylamine, phenol red (PR), cresol red (CR), bromothymol blue (BTB), solvents ($CDCl_3$, tetrahydrofuran, toluene), and sulfur dioxide were purchased from SigmaAldrich and used as received. Pellets of catalyst support γ-alumina was purchased from AlfaAesar and dried overnight under vacuum at 120°C before use. (3-Glycidyloxypropyl)trimethoxysilane (GPMS) was purchased from Gelest. 99.5% Carbon dioxide was purchased from Penn State gas supplies and used as received.

Instrumentation

Photographs were acquired using a Samsung digital camera. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded using a Bruker 300 MHz NMR spectrometer at room temperature. Proton chemical shifts are expressed in parts per million (ppm) and referenced to residual protio content in the NMR solvent ($CDCl_3$, δ 7.24 ppm, DMSO-d^6 δ 2.50 ppm). Carbon nuclear magnetic resonance spectra (^{13}C NMR) were recorded on a Bruker 300 MHz NMR spectrometer at room temperature. The carbon chemical shifts are expressed in parts per million (ppm) and are referenced to the carbon resonances of the NMR solvent ($CDCl_3$, δ 77.23, DMSO-d^6 δ 39.52 ppm). The ATR-IR spectra were recorded on a Bruker IFS 66/S spectrometer. The in situ IR spectroscopic analysis was carried out on an ASI react-IR 1000 Reaction Analysis System. UV-visible spectra were recorded on an Evolution 220 spectrophotometer from ThermoFisher Scientific. The thermogravimetric analysis was carried out using a TGA Q50 probe from Micromeritics, equipped with a Pfeiffer Vacuum Mass Spectrometer. Elemental analysis was carried out by Atlantic Microlab Inc.

Synthetic procedures

Physical immobilization of amino alcohols on γ-alumina. In a typical reaction, 10 mmol of tertiary amino alcohol was dissolved in 15 mL dry tetrahydrofuran, followed by the addition of 2 g of dried alumina pellets. The alumina pellets were soaked in the solution for 48 h under N_2. The volatile content was then removed in a rotary evaporator. The amino alcohol content was analyzed by thermogravimetry coupled with mass spectroscopy. The wt.% amino alcohol loadings observed were 19.6 for TEA-Al_2O_3, 14.3 for MDEA-Al_2O_3, and 12.5 for DMEA-Al_2O_3.

Chemical grafting of amino alcohols on γ–alumina. In a typical reaction, 15 mL dry toluene was added to 5 g dried alumina pellets under N_2, followed by drop-wise addition of (3-glycidyloxypropyl) trimethoxysilane (1.2 mL, 5.4 mmols). The reaction mixture was heated overnight at 110°C, under N_2 atmosphere, followed by vacuum at 110°C for 1 h. The resulting pellets were washed twice with 5 mL of dry toluene to remove any unreacted reagent. The amount of surface grafting was calculated by thermogravimetric analysis. The resulting pellets were then reacted with an excess of the amine (54 mmols, 5 equiv.). The reaction mixture was refluxed for 72 h under N_2. The volatile fractions were removed under vacuum and the resulting material was washed three times with 5 mL of dry tetrahydrofuran to remove the unreacted amine. The product obtained was then heated overnight at 100°C under vacuum, to remove any leftover amine. The amino alcohol grafted pellets were further characterized using FT-IR and thermogravimetric analysis. The wt.% amino alcohol loadings observed were 20.76 for TEA-Al_2O_3 and 16.15 for MDEA-Al_2O_3.

Procedure for preparing the colorimetric sensors. In a typical process, 1 g dry alumina beads were presoaked in 10 mL tetrahydrofuran solution containing 10 mmols of an amino alcohol for 48 h, at room temperature. Then 0.1 mL of a 1 M tetrahydrofuran solution of the pH indicator was added into this mixture. The alumina beads were soaked into the indicator solution for further 30 min and then filtered and dried to obtain the colorimetric sensors.

The covalently grafted amino alcohol beads were soaked in a 10 mL tetrahydrofuran solution containing the indicator (0.01 M) for 30 min followed by filtration and the removal of volatile fractions under vacuum.

For visual detection, the sensors were exposed to known amounts of the gas (SO_2, CO_2, and CO_2 pre-saturated with water vapor) in N_2 atmosphere.

Elemental analysis for SO_2 binding. Elemental analysis was carried out after passing pure SO_2 into neat MDEA for 10 min at a flow rate of 0.5 mL sec^{-1}. Values observed: C 34.13, N 7.96, H 7.62, S 15.44. Calculated: C 32.78; N, 7.64; H, 7.15; S, 17.50 for equimolar SO_2 binding. These results indicate ~1: 0.84 mol ratio of MDEA:SO_2.

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Notes and references

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