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Molecular Design of Intercalation-Based Sensors. 2. Sensing of Carbon Dioxide in Functionalized Thin Films of Copper Octanediylbis(phosphonate)

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Self-assembled thin films of layered copper alkanediylbis(phosphonates) retain the amine-specific intercalation chemistry of the corresponding microcrystalline solids. Aliphatic and aromatic amines bind in a 1:1 ratio to coordinatively unsaturated copper ions in anhydrous $Cu_2(O_3P(CH_2)_8PO_3)$; and by selecting an amine with an appropriate functional tail group, a chemically and sterically well-defined interlamellar binding site for CO_2 is created. Powder X-ray diffraction, Fourier transform infrared spectroscopy, and solid-state NMR experiments were used to study the intercalation of 3-aminopropanol, (3-aminopropyl)methyldihydroxysilane, and *p*-xylylenediamine, and their reversible reaction with CO_2 to form carbonates and carbamates, respectively. By growing these films on the electrodes of a quartz crystal microbalance device, a sensor can be fabricated for monitoring CO_2 in gas streams at concentrations of 0.5−19% (v/v). A Henrian response (frequency change directly proportional to CO_2 partial pressure) was observed, and the time required for equilibration of these devices with CO_2, using 5-layer films, was 3−4 min. Effective diffusion coefficients for CO_2 in the films were determined using a dual-transport model and were found to be in the range (6−9) $\times 10^{-9}$ cm^2/s.

Carbon dioxide, as both a reactant in and a product of large-scale reactions, is the focus of much current research activity. Millions of tons of carbon dioxide are used every year in the carbonated beverage industry and for the production of carbonates, carboxylic acids, carbon monoxide, and urea, and it is a natural byproduct of ammonia production, grain fermentation, natural resevoirs, and chemical and petroleum operations. The need for carbon dioxide sensors for process control and especially for environmental monitoring is the driving force in this area of analytical research. Fast, quantitative, and reliable carbon dioxide sensors are also needed in anesthesiology and physiology, for measuring cardiovascular system exchange rates, and for determining the concentrations of blood gases during surgery.

Most of the currently available sensors for carbon dioxide are electrochemical, using either potentiometric solid-state electrodes or the amperometric Clark electrode.[1] The Clark electrode measures changes in current as the analyte is depleted from solution covered by a gas-porous membrane at constant applied voltage. Similarly, in designs by Stow[2] and Severinghaus,[3] a constant current is applied and the change in potential caused by a pH change, which results from CO_2 transport into the cell, is monitored. Related devices use polymer electrolytes instead of liquid solutions.[4,5] Fiber-optic sensors, which monitor the absorption spectrum of acid−base indicators in a solution[6] or immobilized in plastic[7] or polymer membranes,[8,9] have been described. Solid-state sensors detect a change in ionic conduction (HCO_3^-,[10] Na^+,[11,12] or Mg^{2+} [13]) of a solid electrolyte, which is caused by sorption of carbon dioxide, sometimes in the presence of water or oxygen. Two sensors that use quartz crystal microbalance (QCM) devices monitor the reaction between CO_2 and an amine incorporated into a polymer film.[14,15] Some of the operating characteristics of these sensors are summarized in Table 1. Regardless of sensor type, interferences for amperometric and potentiometric sensors include water vapor, oxygen, hydrogen, and ammonia. Many of these sensors are also sensitive to the water content of the electrolyte solutions or polymer electrolytes.

Reactions of Carbon Dioxide with Alkylamines, Alcohols, and Silanols. Carbon dioxide, although often regarded as an unreactive molecule, does combine rapidly with some organic compounds, notably alcohols and amines, at ordinary temperatures and pressures. Some understanding of these reactions in the gas phase has been gained through ion cyclotron resonance experiments.[16−19] These reactions are essentially acid−base

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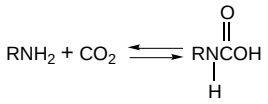
Table 1. Properties of Some CO_2 Sensors

sensing method	useful range	temp of operation	response time	ref
absorbance	0−10%	ambient	90 s	6
absorbance	0−10%	ambient	60 s (air) 2−8 min (H_2O)	9
absorbance	0−40%	40°C	96−120 s	7
absorbance	4 μM−10 mM (in solution)	ambient	<60 s	8
mass change	50−10 000 ppm	40−70 °C	minutes	14
mass change	1.8−16%	20−40 °C	30 s	15
amperometric	3−15%	ambient	20 s	4
amperometric	0−10%	ambient	60 s	5
emf (K_2CO_3)	9 ppm−12%	848−1298 °C	seconds	10
emf (Na_2CO_3)	4 ppm−40%	550 °C	8 s	11
emf (Na_2CO_3, $NaHCO_3$, NaOH)	100 ppm-10%	450 °C	minute	12
emf (Mg^{2+}) in zirconium phosphate	0.5−60%	300−500 °C	seconds	13

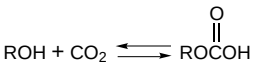
equilibria, but the acidities of the alcohols and amines are reversed from those measured in solution, due to the absence of solvent interactions that stabilize charged species. In the gas phase, inductive effects that stabilize charge centers through the polarizability of substituents are more significant. The electron affinity of the oxygen atom in an alcohol, for example (and therefore the ease with which it releases a proton), is increased by larger alkyl groups, which lower the potential energy of the localized charge on oxygen through induced dipoles. Thus, ethanol is more acidic than methanol in the gas phase, and its electron affinity is higher by several kilocalories/mole.[17] Similar effects have been observed with amines[18] and silanols.[19]

The interaction of CO_2 with primary amines is important in industrial as well as biological applications. Amines are used in industry to remove carbon dioxide from gas streams and in the production of urea and urethanes. The equilibrium between amines, CO_2, and carbamates is represented by reaction 1. This reaction has been studied in solution,[20] but not in the gas phase.



(1)

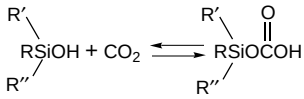
Carbon dioxide combines with alcohols, forming carbonates as in reaction 2. Faurholt and co-workers examined the rapid



(2)

equilibria of the alcohol−bicarbonate (CO_2)−alkyl monocarbonate system in a variety of media, and more recent work has described other alkyl monocarbonate systems in solution.[21] As noted above, the order of increasing acidity is reversed in the gas phase, so that ethanol is more reactive than methanol, but quantitative data on reaction rates are currently unavailable.

The reactions of CO_2 with the surface hydroxyl groups of silica, in zeolites and on mica surfaces, have been studied,[22] and the formation of carbonate species has been monitored by chromatography, mass spectroscopy, and temperature programmed desorption. One of the proposed mechanisms for the separation of carbon dioxide from other gases using chromatographic silica and zeolites is carbonate formation with hydroxyl groups on the surfaces. As noted above, the reactivity of silanols is similar to that of alcohols in the gas phase and depends on the alkyl substitution of the molecule. It has been found that silanols are more acidic than the corresponding alcohols, because silicon is less electronegative than carbon and therefore stabilizes the added electron on oxygen.[19] A possible reaction scheme for an alkylhydroxysilane reaction with CO_2 is



(3)

In the work described here, three receptor molecules that bind CO_2 have been studied as the active elements of QCM-based sensors: an amine, an alcohol, and a silanol. These receptors are bifunctional molecules that can be intercalated into microporous copper octanediylbis(phosphonate) thin films; at one end of the molecule is an amine group that binds to vacant copper coordination sites; at the other is the "business" end of the receptor, a functional group that binds carbon dioxide reversibly as it diffuses into the film.

EXPERIMENTAL SECTION

Reagents. Dilutions of carbon dioxide utitlized high-purity CO_2 gas (Matheson Co., East Rutherford, NJ) mixed with argon. (3-Aminopropyl)methyldiethoxysilane was obtained from Gelest, Inc. All other chemicals used were analytical grade and were obtained from Aldrich Chemical Co., Inc. (Milwaukee, WI).

Instrumentation. *Solid-State NMR.* Spectra were acquired on a Chemagnetics CMX-300 operating in the quadrature mode at 292 K. The resonance frequencies for ^{13}C, ^{29}Si, and ^{1}H are 74.781 093, 59.0724 49, and 297.3720 MHz, respectively. Spin rates for MAS and CPMAS experiments were between 3.0 and 4.0 kHz. Optimized contact times for $^{1}H \rightarrow {}^{29}Si$, and $^{1}H \rightarrow {}^{13}C$ CPMAS experiments were 8 and 4 ms, respectively. The rf field strength was 50 kHz for all experiments. The relaxation delay for the ^{13}C Bloch decays (with ^{1}H decoupling) and CPMAS experiments, and the ^{29}Si CPMAS was 4 s.

Quartz Crystal Microbalance (QCM) Measurements. QCM devices (9 MHz) were used to detect the concentration of CO_2 in

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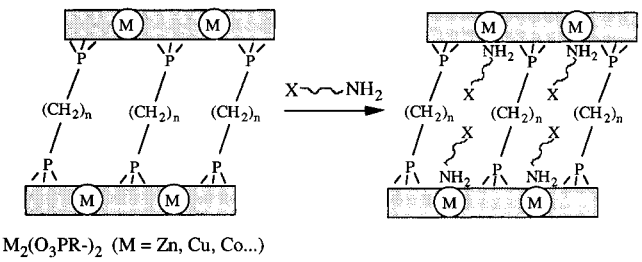
an argon carrier stream, using the experimental configuration described in the accompanying paper.[23]

Preparation of Copper Phosphonate Compounds and Intercalation with Bifunctional CO_2 Receptors. Microcrystalline powder samples of $Cu_2(O_3P(CH_2)_8O_3P)\cdot 2H_2O$ and $Cu(O_3PC_2H_5)\cdot H_2O$ were prepared from the corresponding acids according to literature methods[24] and dehydrated thermally. The solids were ground to a fine powder in an agate mortar and pestle, and 0.5 g portions were put into 10 mL vials. These were dried in an oven for several hours at a temperature appropriate to generate the dehydrated compound [175 °C for copper ethylphosphonate, and 125 °C for copper octanediylbis(phosphonate)]. Upon dehydration, the solids changed in color from pale blue to very pale green. The freshly dehydrated solids were suspended in 25 mL of absolute ethanol, and 1−1.5 mL of the receptor compounds was added dropwise with stirring. Suspensions made in this way were covered and stirred for several days. *p*-Xylylenediamine (*p*XDA; 0.5 g), which is a solid, was dissolved in 25 mL of absolute ethanol, and this stock solution was added to the copper phosphonate suspensions for interclation studies. This compound is sensitive to air, and the solution was therefore prepared in a glovebox and stored under argon.

The bulk solids intercalated with 3-aminopropanol (APA) became dark blue within hours, but the samples treated with the other (bulkier) receptor molecules took longer to react and were left in contact with the solution for several days. The solids were filtered immediately prior to use, washed several times with absolute ethanol, and allowed to air dry briefly. The (3-aminopropyl)methyldiethoxysilane sample was washed with absolute ethanol and allowed to stand for several hours in 95% ethanol in order to hydrolyze the ethoxy groups, thereby converting the intercalated receptor molecule to (3-aminopropyl)methyldihydroxysilane (APMDHS). The samples were ground with a spatula and stored in capped vials. Their blue color did not appear to fade over time (many weeks).

Intercalation of CO_2 Receptors into Thin Films of $Cu_2[O_3P(CH_2)_8PO_3]$. The intercalation of thin films of copper octanediylbis(phosphonate), grown on QCM devices, with receptors for CO_2 followed procedures similar to those used with the powder samples. Five monolayers of $Cu_2[O_3P(CH_2)_8PO_3]\cdot 2H_2O$ were assembled onto the gold electrodes of QCM devices under conditions described previously.[25] The devices were then heated in an oven for several hours at 200 °C in order to remove coordinated water. They were removed from the oven and placed into vials containing several milliliters of the receptor solutions, as described above. The samples were generally left in contact with the solution for one or more days in order to ensure complete reaction. Immediately prior to use, the quartz crystals were removed from the solutions, rinsed with absolute ethanol, and dried in a stream of flowing argon. The silanol-treated crystal was washed with absolute ethanol, dried in argon, and placed in a vial containing 95% ethanol in order to hydrolyze the ethoxy groups. After several hours, this crystal was removed, rinsed with 95% ethanol, and blown dry with argon.

Scheme 1. Intercalation of a Divalent Metal Phosphonate Salt by a Bifunctional Receptor Molecule[a]



[a] The amine end of the molecule coordinates the metal ion.

RESULTS AND DISCUSSION

Scheme 1 shows the general strategy used in this study to create an intercalation-based sensor for CO_2. The intercalation of amines into divalent metal phosphonate salts is well documented in the literature.[24,26,28] Depending on the nature of the metal and the bis(phosphonic acid) used to prepare the compound, the intercalation reaction exhibits varying degrees of size and shape selectivity. With large pillaring groups (R), such as aryl groups, the binding site is restricted to small Lewis bases such as ammonia and water. Less restrictive alkyl pillars, particularly in the copper salts, permit intercalation of the larger bifunctional receptor molecules used in this study. The head group of this molecule, a primary amine, coordinates the metal ion. The tail group (X) and the length of the pillaring group (R) are chosen appropriately to define the size and chemical environment of the interlamellar binding site for the analyte molecule of choice. In light of the reactions discussed above, a diamine, an aminoalcohol, and an amine-terminated alkyldihydroxysilane were studied as receptor molecules for CO_2.

Preparation and Characterization of Copper Phosphonate Solids Intercalated with Bifunctional Receptor Molecules. The intercalation reactions of *p*XDA, APA, and (3-aminopropyl)-methyldiethoxysilane, the precursor to APMDHS, were studied with two bulk copper phosphonate salts, $Cu_2(O_3P(CH_2)_8O_3P)$ and $Cu(O_3PC_2H_5)$. Powder X-ray diffraction (XRD) and solid-state NMR were used to monitor the reaction of CO_2 with the receptor molecules intercalated into $Cu(O_3PC_2H_5)$. The copper octanediylbis(phosphonate) samples were examined by FT-IR and by elemental analysis in order to study the steric requirements of the receptors in a compound where the extent of layer expansion was restricted by the length of the n-octanediyl "pillars".

Anhydrous $Cu(O_3PC_2H_5)$ was found by powder XRD to have a layer spacing of 10.75 Å, in good agreement with the literature value (10.78 Å).[26] Computer-generated space-filling models of *p*XDA show that its length is ~9.0 Å. XRD patterns of the sample intercalated with *p*XDA showed a mixture of the original phase and two new phases with layer spacings of 12.9 and 20.5 Å, possibly corresponding to structures with single (or interdigitated) and bilayer *p*XDA molecules, respectively. In the former case,

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(24) (a) Zhang, Y-P.; Cleafield, A. *Inorg. Chem.* **1992**, *31*, 2821. (b) Wang, R.-C.; Zhang, Y-P.; Hu, H.; Frausto, R. R.; Clearfield, A. *Chem. Mater.* **1992**, *4*, 864. (c) Frink, K. J.; Wang, R-C.; Colon, J. L.; Clearfield, A. *Inorg. Chem.* **1991**, *30*, 1438; (d) Zhang, Y-P.; Scott, K. J.; Clearfield, A. *Chem. Mater.* **1993**, *5*, 495; Zhang, Y-P.; Scott, K. J.; Clearfield, A. *J. Mater. Chem.* **1995**, *5*, 315.
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(28) Cao, G.; Mallouk, T. E. *Inorg. Chem.* **1991**, *30*, 1434.

the *p*XDA molecule would have to be slightly tilted and/or interdigitated with spacers or intercalant chains from the adjacent layer. In the latter case, the layer spacing is consistent with an end-to-end bilayer stacking arrangement of the diamines. The sample intercalated with APA showed an additional phase with a interlayer spacing of 12.0 Å, and the APMDHS-intercalated sample contained a new phase with interlayer spacing of 16.4 Å. These values are in reasonable agreement with the increases in layer spacings reported for the intercalation of alkylamines into zinc and cobalt phosphonates.[24,28]

For a fully extended all-trans conformation of an alkyl chain, the length changes by 1.27 Å per methylene group.[27] In the case of the zinc and cobalt compounds, this value was lower (1.15 Å/CH_2) or higher (1.48 Å/CH_2) for the intercalated structures if the amine chains were interdigitated or stacked as bilayers, respectively.[28] In light of this information, the 2 Å increase in the APA-intercalated solid suggests an interdigitated arrangement. For APMDHS, this structure is unlikely, as the space between adjacent intercalant molecules contains the methyl and two hydroxy groups of the silane. This intercalation compound must therefore have a bilayer arrangement, which leads to the larger change in layer spacing (5.5 Å) upon intercalation.

The thin films used in the sensor devices were prepared from 1,8-octanediylbis(phosphonic acid), so anhydrous $Cu_2(O_3P(CH_2)_8O_3P)$ was prepared and intercalated with APA, *p*XDA, and APMDHS. CHN analysis shows that intercalation is less than complete in all cases. $Cu_2(O_3P(CH_2)_8O_3P)$ itself gave values of 25.21% C and 4.57% H, compared to theoretical values of 24.19% C and 4.03% H. For the *p*XDA-intercalated sample, expected values were 43.05% C, 6.02% H, and 8.37% N, and the values found were 31.32% C, 4.90% H, and 2.99% N, corresponding to filling of ~36% of the available sites (assuming one molecule per copper atom). For the smaller APA molecule, the expected values were 30.71% C, 6.26% H, and 5.12% N, and the analytical results were 29.12% C, 5.56% H, and 3.48% N, corresponding to intercalation into ~68% of the available sites. The APMDHS sample returned values of 26.26% C, 4.61% H, and 0.96% N compared to theoretical values of 30.23% C, 6.66% H, and 4.41% N, indicating coordination at only ~22% of the available sites. These analytical data suggest that steric factors restrict access of the larger receptor molecules to the bulk of the solid and are consistent with previous observations of slow intercalation reactions by bulky molecules.[29]

The presence of the receptor molecules was confirmed by infrared spectroscopy of anhydrous $Cu_2(O_3P(CH_2)_8O_3P)$ and its intercalation compounds. Upon intercalation, the spectra (Figure 1) show the appearance of absorption bands that correspond to receptor vibrational modes in the region 3400−3000 cm^{-1}. In the *p*XDA sample, absorbances for the coordinated amine group can be seen in the longer wavelength part of this region (3150−3000 cm^{-1}). Also in this region are the stretching bands for the hydroxyl groups of the alcohol and silanol molecules, which overlap somewhat with the amine stretching bands. Amine combination bands appear as broad absorbances between 2800 and 2000 cm^{-1}, and C−N stretching accounts for the broadening of peaks in the C−C region (1250−900 cm^{-1}). The silanol spectrum also shows the presence of the Si−CH_3 scissor mode at 1423 cm^{-1} and Si−OH and Si−CH_3 deformation modes at 829 and 814 cm^{-1}, respectively. Unhydrolyzed Si−OCH_2CH_3 groups would appear as sharp absorbances in the 1250−999 cm^{-1} region, and their absence is taken as an indication of complete hydrolysis to form intercalated APMDHS. Infrared peak assignments are given in Table 2.

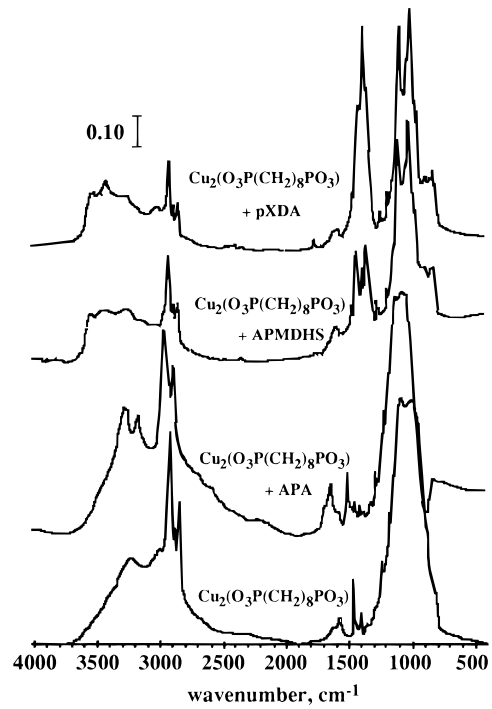

Figure 1. FT-IR spectra of $Cu_2(O_3P(CH_2)_8PO_3)$, and the same sample intercalated with APA, *p*XDA.

Table 2. Infrared Spectral Assignments for $Cu_2(O_3P(CH_2)_8PO_3)$ and Its Intercalation Compounds

	peak wavenumber, cm^{-1}			
mode	no intercalant	+ APA	+ *p*XDA	+ APMDHS
H_2O	3150−3350			
$\nu_{as}(CH_2)$	2928	2927	2928	2927
	2906 (sh)	2906 (sh)		2906 (sh)
$\nu_s(CH_2)$	2852	2851	2853	2852
CH_2 def bending	1468	1468	1468	1468
CH_2 def scissor	1410	1410	1412	
CH_2 wag	1248	1248	1247	1248
	1183	1183	1183	1184
$\nu_{as}(PO_3)$	1093	1092	1096	1092
	1067	1067	1067	1067
$\nu_s(PO_3)$	1011	1014	1008	1009
	978	979 (sh)	979 (sh)	979 (sh)
$\nu_{as,s}(R-NH_2)$ coordinated		3250−3100	3150−3000	33250−3000
$\nu_{as,s}(R-NH_2)$ free		3138	3500−3200	
ν(C−OH)		3400−3000		
ν(Si−OH)				3550−3200

[a] sh, shoulder.

Observation of Carbamate and Carbonate Formation in $Cu(O_3PC_2H_5)$ by Solid-State ^{13}C and ^{29}Si NMR. Intercalated $Cu(O_3PC_2H_5)$ samples were studied by solid-state magic angle spinning NMR in order to observe changes in the receptor molecules upon exposure to CO_2. The carbonate and carbamate equilibria are rapidly reversible, and a CO_2 overpressure was therefore required during NMR spectral acquisition. Spectra were first obtained under ambient conditions, and the samples were

(29) Aoki, K.; Brousseau, L. C., III; Mallouk, T. E. *Sens. Actuators B* **1993**, *14*, 703.

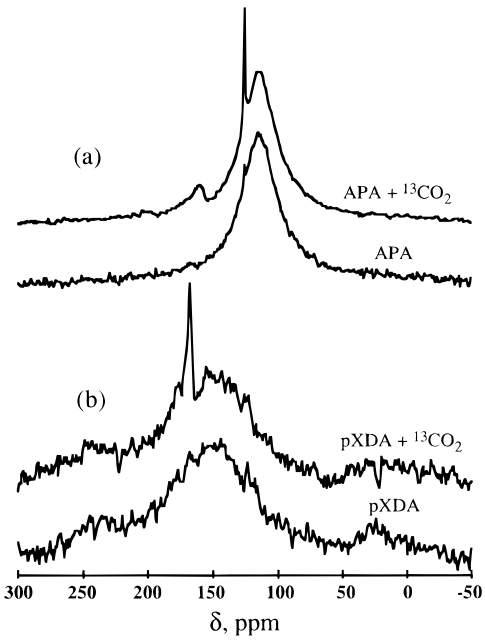

Figure 2. (a) ^{13}C single-pulse MAS-NMR spectra of $CuO_3PC_2H_5$ intercalated with APA, with (upper) and without (lower trace) ^{13}C-labeled CO_2; (b) ^{13}C CPMAS-NMR spectra of $CuO_3PC_2H_5$ intercalated with *p*XDA, with and without ^{13}C-labeled CO_2.

then sealed under ~1 atm of CO_2. In the case of APA and *p*XDA, $^{13}CO_2$ was used. The binding of CO_2 to intercalated APMDHS was investigated using the ^{29}Si nucleus, which has sufficient natural abundance to be observed without isotopic enrichment.

^{13}C spectra of $Cu(O_3PC_2H_5)$−APA with and without added $^{13}CO_2$ are compared in Figure 2a. These spectra were obtained using a single pulse sequence with proton decoupling during acquisition, using a Doty probe assembly and a pulse delay of 4.00 s. The sample without CO_2 (bottom) is dominated by the background absorbance of the rotor inserts, which overwhelms the aliphatic carbon resonances expected at ~20 ppm.[30] Although natural-abundance ^{13}C in $Cu(O_3PC_2H_5)$−APA cannot be observed above the background, the sample containing $^{13}CO_2$ clearly shows a carbonate resonance at 161 ppm, as well as the sharp resonance of free $^{13}CO_2$ at 125 ppm.

^{13}C spectra of $Cu(O_3PC_2H_5)$−*p*XDA are shown in Figure 2b. These spectra were acquired using a cross-polarization pulse sequence, with a Chemagnetics probe. Again the rotor background (bottom) dominates the spectrum of the sample without added $^{13}CO_2$, and natural-abundance ^{13}C in $Cu(O_3PC_2H_5)$−*p*XDA gives signals that are too weak to be observed. When the sample is sealed under $^{13}CO_2$ however (top), the carbamate peak appears above the rotor background as a strong signal at 168 ppm. Note in this case that free $^{13}CO_2$ cannot be observed, because the spectrum is acquired by cross-polarization from ^{1}H to ^{13}C.

^{29}Si NMR spectra of $Cu(O_3PC_2H_5)$−APMDHS are shown in Figure 3. The sample without carbon dioxide (bottom) shows only a single resonance of the silicon atom at −24 ppm [$RSi(OH)_2(CH_3)$].[30] In the presence of CO_2, however (top), new peaks appear. The upfield shift, relative to the free receptor molecule, indicates the formation of an Si−O−X linkage, where X is an element or group that is less electronegative than H. This shift is consistent with the formation of Si−O−CO_2H groups, which

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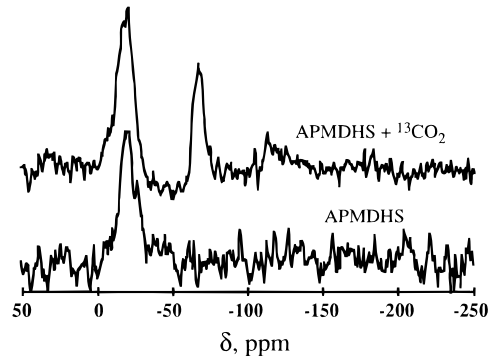

Figure 3. ^{29}Si CPMAS-NMR spectra of $CuO_3PC_2H_5$ intercalated with APMDHS, with and without ^{13}C-labeled CO_2.

are the silicon analogues of the carbonate groups formed with alcohols. The two new resonances are tentatively attributed to the silanol receptor groups binding 1 (−65 ppm) and 2 (−108 ppm) equivalents of CO_2, respectively.[31]

Observation of Carbon Dioxide Reactions in Copper Phosphonate Thin Films Using a Quartz Crystal Microbalance. The concentration range of CO_2 studied with derivatized QCM devices (0−20%) was based upon possible practical applications for the sensors, including the detection of respiratory levels, 3.5−5%.[32] Experimental durations were chosen that allowed for complete saturation of the response of each device by the analyte mixture. After sufficient time, the flow of CO_2 was stopped and the device was allowed to re-equilibrate under flowing argon. Runs for each device were performed consecutively, without removal of the device from the cell, as complete reversal of the response was obtained. As a control experiment, QCMs derivatized with five layers of $Cu_2(O_3PC_8H_{16}PO_3)$ were exposed to 18% CO_2 and showed no response. The devices were also exposed to gaseous water, hydrogen, and oxygen and showed a response with water only. The issue of water interference is discussed below.

Carbonate Formation with APA. For a QCM device prepared with five layers of $Cu_2(O_3PC_8H_{16}PO_3)$−APA, the response to CO_2 is rapid initially and then slows to a relatively constant rate as the process becomes limited by diffusion through the film. The time required to reach saturation is dependent on analyte concentration, but in all cases is less than 3 min. A typical response curve is shown in Figure 4a. The device returns to its original resonance frequency for all concentrations, indicating reversibilty of carbonate formation and good stability of the intercalated receptor molecule under conditions of the experiment. Higher concentrations of CO_2 gave the same response as the 9% case shown in Figure 4a, and the saturation mass change corresponded to binding of 2.7×10^{-9} mol. The theoretical amount, calculated from the mol of $Cu_2(O_3P(CH_2)_8PO_3)$ (assuming one molecule of APA per copper atom) in the film, is 2.6×10^{-9} mol. The agreement with the observed saturation limit for CO_2 intercalation is excellent. The 1:1 receptor:Cu ratio implies that the binding of alkylamines to the second vacant site of the copper ions is much weaker than the first and that the second ligand, if it binds at all, is either washed off in the rinsing step or removed in the initial purge phase of the QCM experiment.

As is seen in the inset of Figure 4a, the response of the device over the range of concentrations studied is linear through the

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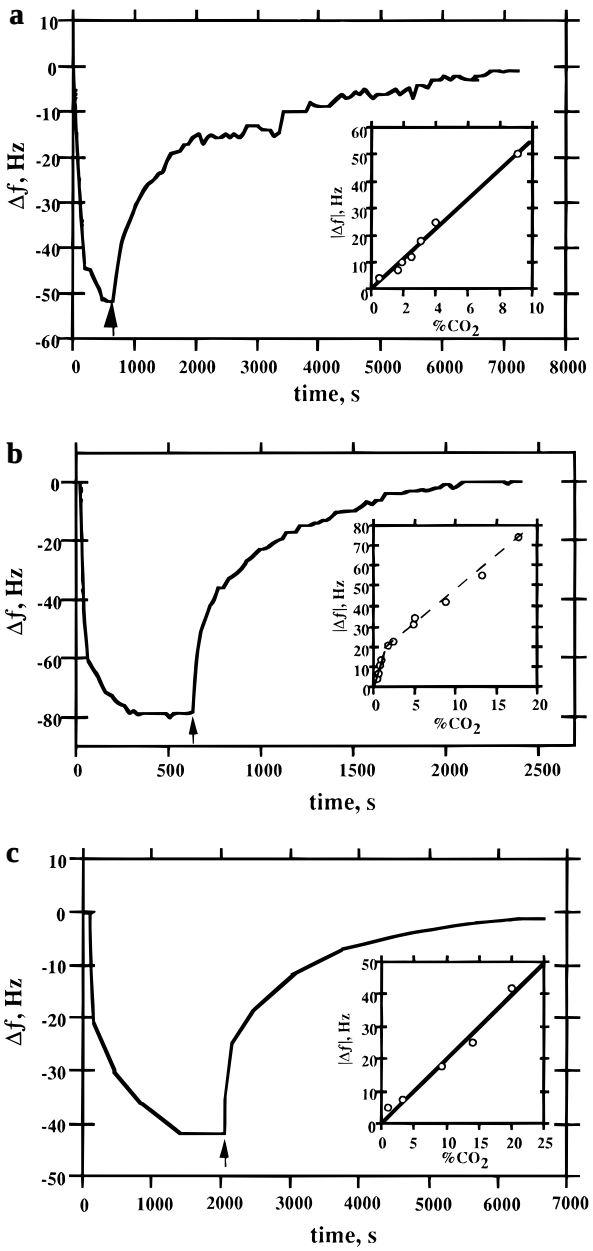

Figure 4. Response curves for QCM devices derivatized with five-layer $Cu_2(O_3P(CH_2)_8PO_3)$ thin films: (a) 9.1% CO_2, film intercalated with APA; (b) 17.7% CO_2, film intercalated with APMDHS; and (c) 20.0% CO_2, film intercalated with *p*XDA. Ar purge was initiated at the arrow in each plot. Insets show plots of limiting $|\Delta f|$ vs % CO_2 for each device.

origin, with a slope of 5.5 Hz/% CO_2 ($R = 0.99$). The limit of detection (LOD) can be estimated as three times the root mean square variation in reproducibility of QCM runs, which is ±1 Hz. This estimate gives a LOD of ~0.6% CO_2. Because of the very small frequency change observed at 0.6%, lower concentrations were not examined. These results indicate that the response of the device is limited by the amount of receptor present, i.e., the number of layers of metal phosphonate grown. Using the dual-transport diffusion model developed for similar ammonia sensors,[23] the effective diffusion coefficient for CO_2 in these films was found to be 6.1×10^{-9} cm^2/s, assuming a 0.5 μm diffusion length. In this case, uptake of analyte follows simple Henrian behavior, and the permeability is defined as $P = SDc$, where S is the partition coefficient of CO_2 in the film, c is the concentration (volume percent CO_2 in the gas stream), and D is the diffusion coefficient in the film. The partition coefficient, S, is taken from the slope of the plot of Δm vs % CO_2. A plot of P/S vs c is linear through the origin with a slope of D.

Carbonate Formation with APMDHS. Figure 4b shows that the initial response of a five-layer $Cu_2(O_3PC_8H_{16}PO_3)$/APMDHS device is also rapid and reaches a stable resonance frequency within 3 min of exposure to CO_2. The frequency change for the 17.7% experiment corresponds to the binding of 4.1×10^{-9} mol, and represents the saturation limit for this device. As before, concentrations lower than 0.6% gave frequency changes that were too small to be reliably interpreted. For a fully intercalated five-layer film with two OH sites per silane, the theoretical amount of carbon dioxide bound would be 5.2×10^{-9} mol. The observation of a CO_2 response that is intermediate between one and two CO_2 molecules per APMDHS is qualitatively consistent with the ^{29}Si NMR spectra (Figure 3), which show a mixture of single- and double-coordination for the bulk solid. Interestingly, the binding curve with this receptor (inset in Figure 4b) is not linear, consistent with the presence of two interacting binding sites on the same molecule. An alternative explanation, that the silane precursor to APMDHS cannot saturate the binding sites in the film, was eliminated by growing the films from solutions containing both the silane and the bis(phosphonic acid). This procedure gave no appreciable difference in the magnitude of the signal, and the result argues against low mobility of the bulky receptor molecule in the lattice as a cause for the slightly lower than 2:1 stoichiometric response. The reversal reaction demonstrates that the device returns to its original resonance frequency upon purging with Ar. Again, the response to varying concentrations of CO_2 was Henrian (inset in Figure 4b), and the effective diffusion coefficient, 8.6×10^{-9} cm^2/s, was similar to that found with the APA receptor.

Carbamate Formation with pXDA. It was anticipated that the bulky phenyl group might limit access of *p*XDA to the $Cu_2(O_3PC_8H_{16}PO_3)$ film, and therefore the loading step was undertaken after every second layer adsorption cycle. A typical Δf vs time curve for a five-layer film is shown in Figure 4c. The response for 20.0% CO_2 corresponds to 2.2×10^{-9} mol or 85% of the theoretical loading. Higher concentrations gave a similar response, indicating the saturation limit. As with the other receptor molecules, the response is quite rapid, reaching completion in ~4 min, and completely reversible. Henrian sorption behavior was observed, as with the other receptors, and a similar effective diffusion coefficient for CO_2, 6.1×10^{-9} cm^2/s, was also found.

Intercalation of H_2, O_2, and H_2O Vapor. In anticipation of possible interferences, the devices described above were exposed to 4% hydrogen and 4% oxygen mixtures in Ar. Five-layer devices showed an initial decrease in frequency of 1 Hz when exposed to each and then an immediate return to the initial resonance, as can be seen in Figure 5. The application of 15% CO_2 to a QCM device derivatized with a five-layer film of $Cu_2(O_3P(CH_2)_8PO_3)$ but no receptor molecule resulted in a similar response, but the frequency returned to its initial value immediately.

A mixture of water vapor in Ar was prepared by passing a stream of argon through a bubbler containing deionized water, which was kept at 0 °C in an ice bath. This gave a gas-phase concentration of 4.6% (v/v). The response of the *p*XDA device to this vapor is also shown in Figure 5 and is representative of the response of all of the devices. The amount of water taken up by

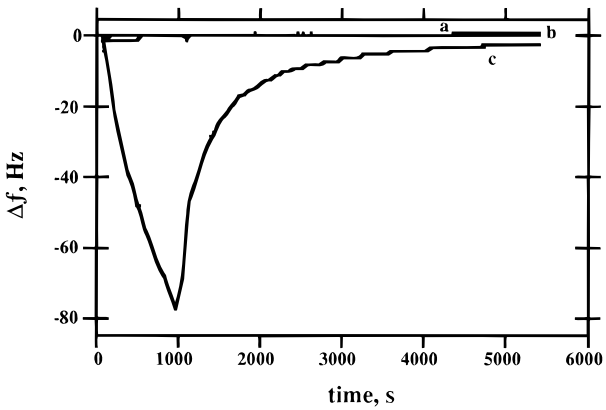

Figure 5. Response curves for the reactions of (a) 4% H_2, (b) 4% O_2, and (c) 4.6% H_2O with QCMs derivatized with five-layer *p*XDA/$Cu_2(O_3P(CH_2)_8PO_3)$ thin films. The devices were purged with Ar after 1000 s.

the films was 9.9×10^{-9} mol, almost 4 times the amount of water that could be accounted for by reacting in a 1:1 ratio with all the receptor molecules in the films. (Note that displacement of a volatile receptor molecules by water should actually cause a frequency increase, or mass decrease.) The resonance frequency returns to the original value after the flow of water vapor is discontinued. This would imply that the increase is due to hydrogen bonding with the receptors or with the copper phosphonate lattice, and the water is weakly bound. A device containing no receptor molecules, exposed to this vapor, showed a simliar response and a mass increase corresponding to 9.0×10^{-9} mol, indicating that binding at copper phosphonate lattice sites is indeed occurring to a significant extent.

CONCLUSIONS

The intercalation of bifunctional receptors APA, APMDHS, and *p*XDA, and their reaction with CO_2 to form carbonates and carbamates, respectively, were observed with copper octanediylbis-(phosphonates) and related thin films. The presence of these receptor molecules in the thin films allows them to be used as the active elements of QCM sensors. These devices allow detection of various concentrations of CO_2, with a response limited by the stoichiometry of binding at metal sites in the films. The response of the devices to CO_2 is linear over a range of gas-phase concentrations. The reactions are reversible at room temperature and low partial pressure, but the "off" rate is slower than the "on" rate. The devices also show a substantial interference with water vapor (a potentially serious problem in anesthesiology applications), but this appears to be mostly a consequence of physisorption to the host films and does not represent the reaction of water with the receptor molecules. This observation suggests that it may be possible, in future experiments, to saturate the water binding sites with stronger ligands, while retaining the affinity of the intercalated receptor molecules for CO_2. In light of the interference seen with water, it remains to be demonstrated, through testing of a wider range of chemically different vapors, that selectivity of these devices to CO_2 is general. Finally, we note that the general design presented here might be extended to other kinds of bifunctional receptor molecules in order to create intercalation-based sensors for other small molecule analytes.

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