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Selective Real-Time Measurement of Styrene Vapor Using a Surface-Acoustic-Wave Sensor with a Regenerable Organoplatinum Coating

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The performance of a coated surface-acoustic-wave (SAW) sensor for monitoring styrene vapor is investigated. The effects of several organic co-contaminants and atmospheric humidity are described, and regeneration of the sensor coating is demonstrated. The dual-SAW delay-line oscillator employs a reagent coating of *trans*-$\mathrm{PtCl_2}$(ethylene)(pyridine) to trap styrene via ethylene substitution. The rate of change of the sensor frequency is used to provide real-time measurement of styrene vapor concentrations. No effect on the response to styrene is observed upon simultaneous exposure to each of several olefin and non-olefin solvent vapors used with styrene in industrial processes. Butadiene, however, presents a reversible negative interference by successfully competing with styrene for reaction with the trapping agent. The response to styrene exhibits a moderate positive humidity dependence. Following prolonged exposure, the original complex can be regenerated in situ by exposure to ethylene gas, permitting repeated use of the sensor. An emphasis is placed on the application of the sensor to workplace air monitoring.

INTRODUCTION

Styrene is used principally for the industrial-scale production of polymer resins and thermoplastics, often in combination with other vinyl monomers such as acrylonitrile, butadiene, or various acrylates (*1*). While industrial surveys have shown that exposure to these monomers during polymer production is minimized by the use of closed reactor systems, transient releases can occur during transfer to and from storage vessels and during maintenance operations (*2*). Subsequent processing of polymer materials can also result in exposure to residual monomers (*3*).

Exposure to styrene is also encountered in the fiber-reinforced plastics (FRP) industry (*2*). In a typical FRP operation, the viscous resin-laden fiber material is sprayed onto a product mold and then manually rolled out to remove entrapped air. The resin contains a high percentage of styrene, along with curing agents, binders and other volatile solvents that off-gas during this process. The most common air contaminants found in the FRP workplace along with styrene are aromatic hydrocarbons (e.g., ethylbenzene and toluene), chlorinated hydrocarbons (e.g., methylene chloride), and aliphatic ketones (e.g., acetone and 2-butanone) (*2*).

Occupational exposure to styrene vapor has been associated with impairment of the central and peripheral nervous systems as well as irritation of the eyes, skin, and upper respiratory tract (*1*, *2*, *4*). Styrene is also weakly mutagenic in vitro and in vivo (*1*, *5*), presumably due to metabolic transformation to styrene 7,8-oxide followed by DNA alkylation (*6*). These data, coupled with findings of increased frequencies of chromosomal aberrations (*7*, *8*) and sister chromatid exchanges (*9*) in the lymphocytes of styrene-exposed workers, suggest the possibility of styrene genotoxicity.

The recently revised Occupational Safety and Health Administration (OSHA) limits for styrene are 50 ppm based on an 8-h time weighted average (8-h TWA) and 100 ppm for short-term exposures (15-min TWA) (*10*). Similar workplace exposure limits are recommended by both the American Conference of Governmental Industrial Hygienists (ACGIH)

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(*11*) and the National Institute for Occupational Safety and Health (NIOSH) (*2*) to protect against the irritant and narcotic effects of styrene exposure.

Given the acute toxicity of styrene, it is desirable to measure workers' exposures continuously. Unfortunately, currently available portable direct-reading instruments lack the degree of selectivity necessary to discriminate between styrene and most of the potentially interfering gases and vapors mentioned above. Thus, a coated surface-acoustic-wave (SAW) chemical sensor was developed to measure styrene vapor continuously in the industrial environment.

The small size, simple design, and excellent sensitivity of this sensor, coupled with the ability to adjust the sensitivity and selectivity (by judicious choice of a chemically sensitive coating layer), make this device attractive for incorporation into miniaturized air-monitoring instrumentation. A wide variety of chemicals have been detected with coated-SAW sensors (*12*), and detection limits in the part-per-billion concentration range have been reported by several authors (*13–15*). However, only limited testing of selectivity in the presence of relevant interferences has been performed (*16*). The effects of other environmental variables, such as ambient temperature and humidity, which are critical to the ultimate performance of the sensor in field applications, have also received little attention.

In the preceding paper we showed that a SAW sensor coated with a mixture of *trans*-$PtCl_2$(ethylene)(pyridine) and poly(isobutylene) (PIB) could provide real-time measurement of styrene vapor over a concentration range of 5–700 ppm, with a calculated detection limit of 0.6 ppm (*17*). The sensor response is based on the increase of the mass of the coating accompanying the displacement of ethylene from the solid platinum–ethylene π-complex and formation of the corresponding styrene complex, *trans*-$PtCl_2$(styrene)(pyridine). The sensitivity to styrene was found to increase with increasing temperature according to an Arrhenius relationship.

In this paper, we present the results of laboratory experiments designed to assess the performance of this sensor as a real-time monitor of styrene vapor. The effects of ambient humidity and other solvent vapors on the response to styrene are investigated and the ability to repeatedly regenerate the coating reagent by treatment with ethylene is demonstrated.

COATING SELECTION CONSIDERATIONS

Selectivity and reversibility are often competing characteristics of a chemical sensor. In the SAW sensor these characteristics are a function of the type of interaction occurring between the analyte gas or vapor and the coating film deposited on the surface of the sensor. While low-energy, spontaneously reversible interactions, such as physical adsorption or absorption, are desirable for extended sensor operation, they generally lack a high degree of selectivity. Higher-energy interactions, such as chemical-bond formation, are more selective but also tend to be less reversible. Sensor coatings designed for this type of interaction would eventually become saturated.

The use of sensor arrays coupled with pattern recognition analysis has been explored as a way to achieve a high degree of selectivity using reversible sensor–analyte interactions (*16*, *18*). In this case, the different sensor coatings need only be partially selective as long as the pattern of responses from the array permits discrimination of the target analyte(s) from potentially interfering chemicals. However, the ultimate discriminating power of the array will still depend on the selectivity of the individual sensors, particularly where mixtures of structurally similar chemicals are involved.

The approach taken in designing chemically sensitive sensor layers will be influenced by the constraints of the particular application. For workplace monitoring over a single workshift, it is feasible to consider nonreversible interactions since the sensor could be replaced or regenerated between sampling periods. For long-term continuous monitoring, reversibility may be a more important consideration.

With the sensor coating employed here, styrene is trapped as a stable product. As a result, the trapping reagent is eventually depleted. However, regeneration of the original trapping reagent is possible, permitting repeated use of the sensor.

EXPERIMENTAL SECTION

Detailed descriptions of the reagent synthesis, sensor fabrication, data aquisition system, test-atmosphere generation apparatus, and coating-deposition method have been presented in the preceding paper (*17*). Only procedures specific to this series of experiments are presented here.

Synthesis. The butadiene-substituted complex $[PtCl_2(pyridine)]_2$(butadiene) was prepared by passing butadiene gas (Matheson) through a refluxing solution of *trans*-$PtCl_2$(ethylene)(pyridine) in methylene chloride for 45 min. Addition of petroleum ether to the cooled solution yielded an orange-yellow precipitate, mp 134 °C (dec). Anal. Calcd: C, 22.6; H, 2.3. Found: C, 22.7; H, 2.2.

The polymer-bound complex, $PtCl_2$(ethylene)(poly(4-vinylpyridine) (nominal formula), was prepared by adding a solution of 34 mg (0.34 mmol based on 4-vinylpyridine) of poly(4-vinylpyridine) (Scientific Polymer Products) in aqueous ethanol to a stirred solution of 200 mg (0.54 mmol) of $KPtCl_3$(ethylene) (Alfa) in aqueous ethanol. A flocculent yellow-white precipitate formed upon addition of the polymer solution. The supernatant was removed following centrifugation and the solid was rinsed twice with ethanol and dried in air. The solid was soluble in methylene chloride and chloroform. No further structural characterization was performed.

Test-Atmosphere Generation. Solvent vapors were generated by passing nitrogen through a bubbler containing the liquid solvent and then into a metered dilution-air stream. For butadiene and vinyl chloride, a syringe pump was used to introduce the pure gas into the air stream. The flow rate, temperature, and relative humidity (RH) of the dilution air were controlled with a Miller-Nelson Research Model HCS-301 controller.

An infrared gas analyzer (Foxboro, MIRAN 1A) was used for continuous verification of gas/vapor concentrations. For experiments involving simultaneous exposure to styrene and each of the other contaminants, the gas analyzer was calibrated for each component of the mixture individually at a wavelength where both chemicals exhibited strong IR absorbance. After a constant concentration of styrene vapor was established, the second contaminant was introduced and the increase in the IR absorbance was used to determine the concentration of the second component.

Trapping Agent Regeneration. Following exposure to styrene, the *trans*-$PtCl_2$(ethylene)(pyridine) was regenerated by exposing the sensor to pure ethylene. The difference frequency decreased rapidly upon initial exposure to ethylene, corresponding to replacement of ethylene for styrene in the complex. Exposure was continued until no further decrease in frequency was observed, which typically required 25–40 min.

RESULTS AND DISCUSSION

Selectivity. The selectivity of the sensor was investigated for both simultaneous and sequential exposures to styrene and each of several other gases and vapors used with styrene in industrial processes. For most experiments a styrene concentration of 50 ppm was used, corresponding to the Occupational Safety and Health Administration (OSHA) limit for occupational exposures (*10*). The concentrations of the other vapors tested were all well in excess of their respective OSHA exposure limits (*10*). The other chemicals examined included toluene, ethylbenzene, 2-butanone, methylene chloride, acrylonitrile, butadiene, methyl acrylate, methyl methacrylate, vinyl acetate, vinyl chloride, and mesityl oxide.

All of the potential interferences were absorbed by the coating film as indicated by an initial negative shift in the frequency of the single oscillator upon exposure and a cor-

Table I. Sensor Response for Exposure to Approximately 50 ppm of Styrene with and without Other Cocontaminants Present at the Indicated Concentrations[a]

trial	co-contaminants	mean response (std dev), Hz/min
1	styrene	43 (8)
	styrene + 2-butanone (300 ppm)	44 (6)
2	styrene	46 (3)
	styrene + dichloromethane (350 ppm)	45 (6)
3	styrene	48 (6)
	styrene + ethylbenzene (250 ppm)	49 (4)
4	styrene	47 (5)
	styrene + toluene (300 ppm)	50 (6)
5	styrene	40 (5)
	styrene + acrylonitrile (120 ppm)	42 (5)
6	styrene	48 (3)
	styrene + methyl acrylate (800 ppm)	45 (3)
7	styrene	52 (4)
	styrene + methyl methacrylate (200 ppm)	53 (4)
8	styrene	53 (5)
	styrene + mesityl oxide (140 ppm)	52 (5)
9	styrene	50 (4)
	styrene + vinyl acetate (135 ppm)	51 (3)
10	styrene	46 (8)
	styrene + vinyl chloride (65 ppm)	42 (8)
11	styrene	42 (9)
	styrene + butadiene (30 ppm)	11 (3)

[a] T = 25 °C, RH = 50%.

responding positive frequency shift upon removal from the atmosphere. These signals were effectively masked by measuring the difference frequency with the reference device coated with PIB. No further change of frequency was observed for exposure to these chemicals, with the exception of butadiene, vinyl acetate, and methyl acrylate. In all cases, the response to styrene was the same before and after exposure to these chemicals.

Exposure to methyl acrylate from 50 to 900 ppm yielded responses ranging from 3 to 28 Hz/min, respectively. For vinyl acetate, exposures ranging from 10 to 275 ppm yielded responses ranging respectively from 2 to 30 Hz/min (*19*). Curiously, butadiene exposure caused a *decrease* in the difference-frequency signal (i.e., an increase in the single oscillator frequency). Exposure to 30 ppm of butadiene caused an initial response of −22 Hz/min (averaged over 15 min); however, the response declined to negligible values after only 45 min of exposure. Raising the butadiene concentration had no effect on the response. A more detailed discussion of the interaction of butadiene with the sensor coating is provided below.

To further examine the selectivity for styrene, the coated sensor was exposed simultaneously to styrene and each of the chemicals listed above. As shown in Table I, with the exception of butadiene, the presence of these other gases and vapors did not affect the response to styrene. The lack of interference by the non-olefin and nonreactive olefin vapors might have been expected, but does provide evidence for an S_N2 (i.e., non-solvent-assisted) mechanism for the reaction with styrene, as reported for similar olefin-substitution reactions in solution (*20–23*). Remarkably, neither vinyl acetate nor methyl acrylate affected the response to styrene, even though they react individually with the trapping agent. This indicates that styrene is exclusively favored in the competition for reaction with the solid.

The selectivity for styrene may be explained by considering the nature of the platinum–olefin bond in these complexes. Bonding between the olefin and the platinum involves donation of electron density from the π-cloud of the olefin to the metal d-orbitals via a σ-bond, as well as back-bonding from the metal to the olefin via a π-bond (*20*). The energies and overlaps of the involved orbitals will determine the strength of the platinum–olefin bond. Meester et al. have determined approximate energies for the highest-occupied and lowest-unoccupied platinum d orbitals in several $PtCl_2$(olefin)(pyridine or NH_3) complexes based on spectroscopic data (*24*). A comparison of these energies with those of the corresponding free-olefin orbitals is shown in Figure 1 for several of the olefins studied here. For the unoccupied orbitals, there is no discernible correlation between the relative reactivities and the relative energies of olefin and platinum orbitals involved: energy differences for styrene, methyl acrylate, and acrylonitrile are all <0.7 eV, and that of vinyl acetate is >1.4 eV. For the occupied orbitals, however, styrene has the closest energy match followed in order by vinyl acetate, methyl acrylate, and acrylonitrile.

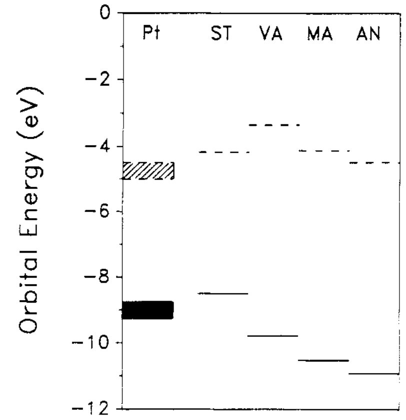
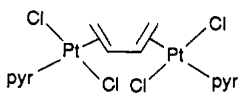


Figure 1. Comparison of approximate energy levels of the highest-occupied orbitals (——) and lowest-unoccupied orbitals (- - -) of free olefins and platinum in *trans*-$PtCl_2$(olefin)(pyridine or NH_3): ST = styrene, VA = vinyl acetate, MA = methyl acrylate, AN = acrylonitrile. Adapted from ref 24 with permission.

Apparently, the σ-bond interaction is more important in determining the relative reactions rates (and product stabilities) for these olefin substitution reactions. This is consistent with our previous results where preferential reaction with vinyl acetate was observed in the presence of methyl acrylate (*19*). The failure of vinyl chloride to react or interfere with the response to styrene is most likely due a combination of poor orbital overlap and the presence of the strongly electron-withdrawing chlorine substituent on the double bond. For methyl methacrylate and mesityl oxide, the additional steric hindrance from the methyl groups on the double bonds undoubtedly contributes to their lack of reactivity.

As noted above, exposure to butadiene caused an initial increase in the single oscillator frequency (decrease in the difference frequency), which corresponds to a decrease in the mass/area of the coating (see eq 1 in ref 17). To further investigate the product of reaction with butadiene, a sample of the butadiene-substituted complex was synthesized by reaction with the $PtCl_2$(ethylene)(pyridine) complex in solution (see Experimental Section). Elemental analysis of the product is consistent with the bridged structure shown below, wherein each double bond is coordinated to a separate platinum moiety (note: the butadiene configuration may be cis or trans). Similar bridged structures involving butadiene complexes with platinum and palladium have been reported (*25*).



Since there is a negligible net mass difference accompanying the substitution reaction, the increase in the single-oscillator frequency observed upon exposure to butadiene is attributed

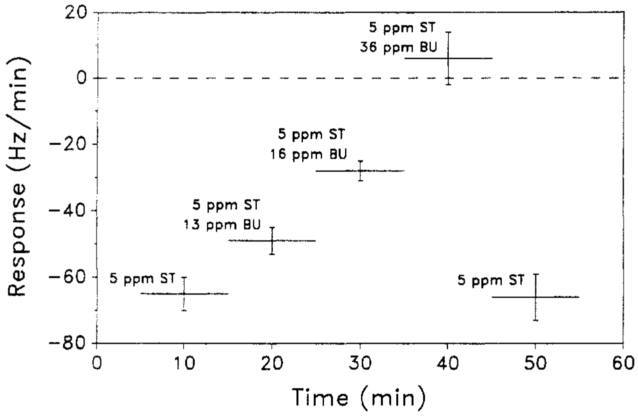


Figure 2. Response to 5 ppm of styrene at 40 °C with varying concentrations of butadiene. Each point represents the mean response for exposures of 10-min duration.

to a slight decrease in the density incurred upon formation of the butadiene complex (note: an increase in the elastic stiffness of the coating would also cause an increase in frequency; however, this outcome seems unlikely given the low modulus of the PIB in the coating). That the response to butadiene declines rapidly may reflect either an unfavorable competition with ethylene or conformational constraints encountered within the solid complex.

Results of additional tests of the effect of butadiene on the response to styrene are shown in Figure 2 for exposure at 40 °C to 5 ppm of styrene and various concentrations of butadiene. The steady-state response decreases as the butadiene concentration increases. At 136 ppm of butadiene the reaction with styrene is completely blocked. Removal of butadiene leads to a recovery of the initial response obtained for styrene alone. Thus, displacement of butadiene from the complex by styrene appears to proceed at a rate similar to that for ethylene.

Attempts to monitor butadiene using *trans*-$PtCl_2$(styrene)(pyridine) as the coating reagent gave a response that was independent of concentration: for exposures ranging from 16 to 150 ppm of butadiene, a constant response of −20 Hz/min (15-min average at each concentration) was observed (note: in this case a decrease in the difference frequency is expected because styrene is displaced by the lighter butadiene).

Humidity Effects. The effects of humidity on the sensor were examined with and without styrene present. Initial tests involved monitoring the single coated-oscillator output with no styrene present during a series of step-changes of relative humidity (RH) over the range of 5–80% RH (25 °C). For each change of RH, the sorption of water vapor caused an abrupt decrease in the frequency over the first few minutes followed by reestablishment of a stable frequency, as observed for the nonreactive organic vapors described above. From 5 to 60% RH a net frequency shift of only −370 Hz was observed, corresponding to a relatively small uptake of water vapor by the coating. Increasing the RH from 60 to 80% resulted in a significantly larger frequency shift (~−560 Hz) than observed at lower RH values. Similar nonlinear sorption behavior has been reported for a polyimide-coated SAW sensor upon exposure to water vapor, although the frequency shifts obtained were about 2 orders of magnitude larger than those seen here (*26*). Upon return to 5% RH, the base line oscillator frequency returned to the preexposure value, confirming the reversibility of water-vapor sorption.

The effect of humidity on the response to styrene was also examined at 25 °C for RH values ranging from 5 to 80%. Figure 3 summarizes the results of several experiments involving a sequence of exposures to styrene at 5, 50, and then 80% RH (solid line in Figure 3), followed by reexposure at 50% and then 5% RH (dashed line in Figure 3). For each change of RH level in the exposure series, the sensor was allowed to equilibrate for several minutes before being exposed to styrene. Responses are presented relative to the initial response at 5% RH, and each point represents the mean relative response for exposures of 15–30 min duration at each of several styrene concentrations in the range of 10–600 ppm. Relative responses are in the ratio 1:1.6:2.2 for operation at 5, 50, and 80% RH, respectively. As shown, no significant hysteresis is observed. The lower response observed upon returning to 5% RH is within experimental error and is attributed to a slight reduction in the surface area of the trapping reagent accompanying repeated exposure to styrene (see below).

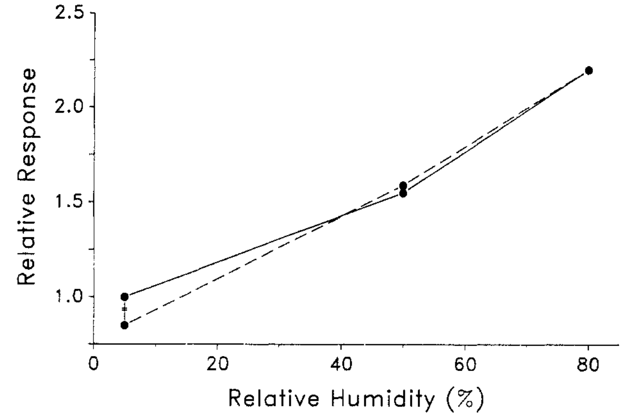


Figure 3. Relative response to styrene at 25 °C for relative humidities (RH) ranging from 5 to 80%. Solid line is for increasing RH and dashed line is for decreasing RH. Each point represents the mean relative response for exposures ranging from 10 to 620 ppm.

The most likely explanation for the observed humidity dependence is an increase in the olefin-substitution reaction rate due to the solvation effect of adsorbed water. Although there are no ionized species involved in the reaction, water would be expected to stabilize the polar pentacoordinate transition state to a greater extent than the square-planar reactant complex. Adsorbed water might also facilitate diffusion of styrene into the solid. Note that the ratio of responses to styrene at 50 and 80% RH (~1.4) parallels the ratio of water vapor uptake by the coating at these RH levels.

An alternative explanation for the increased response is the establishment of an additional, solvent-assisted reaction pathway involving surface-adsorbed water. A similar mechanism was postulated to describe olefin-substitution reactions of *trans*-$PtCl_2$(ethylene)(4-X-aniline) complexes in noncoordinating solvents upon addition of traces of ethanol (*23*)—a reduction in the degree of bimolecular substitution of the bound olefin was suggested as resulting from initial displacement of the olefin by ethanol. If water were displacing ethylene in our complex, however, one would also expect to see a continual decrease in the single-oscillator response at high humidity, which was not observed. Furthermore, interference by other olefins and nonolefins would have been expected if a solvent-assisted mechanism were important. Thus, while this mechanism cannot be ruled out completely, any competition between water and ethylene for coordination to the platinum clearly favors the latter.

Coating Regeneration. As expected, the sensitivity gradually declines upon continued exposure styrene due, in part, to depletion of the unreacted trapping agent. While for low styrene concentrations (i.e., 10 ppm) there was no measurable decline in response over 8 h of continuous exposure, at 50 ppm the response declined by about 20% after 4 h, and at 300 ppm the response declined by about 75% after

Table II. Response to Styrene at 25 and 38 °C (20% RH) of Original Coatings and Multiple Regenerated Coatings[a]

styrene concn, ppm	response, Hz/min			
	original coating	1st regen	2nd regen	3rd regen
	Initial Exposure (25 °C)			
10	17	18	20	21
230	36	32	32	30
625	89	87	86	81
	Reexposure (25 °C)			
10	6	6	8	11
230	24	22	22	20
625	58	53	54	48
	Initial Exposure (38 °C)			
3	31	32	31	32
8	51	61	52	56
50	109	114	94	95
	Reexposure (38 °C)			
3	20	19	18	23
8	34	31	34	29
50	50	56	59	54

[a] Each value represents the mean response for exposures of 15–30 min duration.

4 h. Increasing the amount of coating material initially deposited on the device did not alter the decline in response. Given the apparent dependence of the reaction on the available surface area of the trapping agent (*17*), this result was not unexpected.

Treatment with pure ethylene gas resulted in release of styrene and regeneration of the original complex (note: the structure of the regenerated complex was confirmed by IR spectrophotometry in a separate series of experiments). Table II shows a series of responses (15–30 min averages) measured at 25 and 38 °C that demonstrates the regenerability of the coating reagent. The first column in Table II presents responses for the original coatings at each temperature and illustrates the decline in sensitivity upon reexposure to styrene. Values presented in columns 2–4 were obtained following successive regeneration/exposure cycles. As shown, the responses of the regenerated coatings were virtually the same as those for the original coatings.

Regeneration following prolonged exposure, however, gives a response that is initially higher than that for the initial coating. Figure 4 shows this effect for exposure at 25 °C to 50 ppm of styrene followed by regeneration and reexposure. The response of the original coating remained essentially constant for several hours, dropping to about 80% of the initial response value after 4 h. In this case, the response of the regenerated coating was initially 28% higher than that of the original coating. After several minutes, however, the regenerated-coating response returned to that of the original coating. Similar results were obtained for exposure at 40 °C.

We speculate that reaction with styrene causes an expansion of the crystal lattice of the platinum–ethylene complex that persists after regeneration. This would increase the accessible surface area as well as facilitate diffusion through the solid during the initial phases of the subsequent exposure. Apparently, this effect is not significant at low conversion levels but becomes more important as more of the reagent reacts.

For longer exposures the assumption of catalytic behavior, made in the previous paper for comparison with theoretical rate models (*17*), is clearly no longer valid. As the reaction proceeds, the styrene, as well as the evolved ethylene, must diffuse through an increasingly thick layer of the product platinum–styrene complex. In addition, the ethylene may react with the product layer as it diffuses out of the solid.

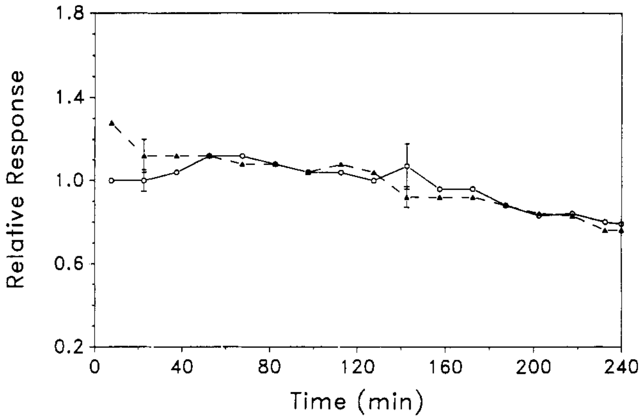


Figure 4. Relative response to 50 ppm of styrene for original coating (○) and regenerated coating (▲) for continuous 4-h exposures. Each point represents the mean relative response determined at 15-min intervals.

Thus, the gradual reduction in the sensor response may result from a combination of these phenomena and a net reduction in reactive surface area of the platinum–ethylene complex. Under these conditions, the so-called unreacted-core model described by Levenspiel (*27*) may be more appropriate for describing the trapping reaction. This model depicts the gas–solid reaction as proceeding from the outer surface of the solid inward, with production of a progressively thicker product shell (the platinum–styrene complex in this case) around a shrinking core of unreacted starting material. The use of this model to predict the behavior of the sensor for prolonged styrene exposure is currently being explored.

An alternative approach being investigated involves the polymer-bound reagent $PtCl_2$(ethylene)(poly(4-vinylpyridine)) as the sensor coating. Preliminary experiments using an uncharacterized sample of this reagent yielded a sensor response of 50 Hz/min for exposure to 50 ppm of styrene, although the response declined fairly rapidly for the thin films examined. Regeneration with ethylene provided a response equivalent to that of the original coating.

CONCLUSIONS

Selective measurement of styrene vapor in the parts-per-million concentration range has been achieved by using a SAW sensor coated with a mixture of *trans*-$PtCl_2$(ethylene)(pyridine) and poly(isobutylene). With the exception of butadiene, which causes a reversible negative interference, co-exposure to each of several relevant olefin and non-olefin interferences does not affect the response to styrene. The high degree of selectivity obtained represents an improvement over portable direct-reading instruments currently used for monitoring styrene in the industrial environment.

Preferential reaction with styrene in the presence of other olefins is consistent with the similarity in the energies of the bonding orbitals of platinum and styrene. The steric properties of the attacking olefin also appear to affect the reactivity with the trapping agent. Further research is needed to determine whether other olefins can be detected selectively based on the size or electron-withdrawing/donating strengths of the olefin substituents. The influence of steric and electronic factors also suggests that altering the substituents on the pyridine and/or ethylene ligands of the trapping agent could be used to adjust the selectivity of the sensor.

Increasing atmospheric humidity from 5 to 80% roughly doubles the response to a given styrene concentration. In practice, a means for monitoring or eliminating ambient humidity would be needed. It should be noted that conventional photoionization detectors exhibit a stronger humidity dependence (*28*), requiring the use of a scrubber to eliminate water vapor upstream from the sensor. A similar technique might be employed for the sensor described here.

At present, the operating time of the sensor is limited by the gradual depletion of the trapping reagent in the coating. The decline in the sensor response over time is apparently related to both the reduction in active surface area and the mass-transfer resistance associated with diffusion of styrene and ethylene through an increasingly thick solid product layer. The trapping reagent can be regenerated after exposure to styrene by treatment with ethylene gas, in situ. For relatively short-term exposures, multiple regenerations are possible with retention of the original coating response characteristics. For prolonged exposure, however, the regenerated coating exhibits initially higher sensitivity than the original coating which is attributed to an expansion of the crystal lattice in the outer layer of the solid following styrene exposure. The use of a polymer-bound trapping reagent with active sites distributed along the polymer backbone may have several advantages over the use of a discrete solid trapping reagent. Preliminary results using a poly(4-vinylpyridine) analogue of the platinum–ethylene π-complex demonstrate the feasibility of this approach.

Registry No. $[PtCl_2(pyridine)]_2$(butadiene), 127086-68-4; $KPtCl_3$(ethylene), 12012-50-9; styrene, 100-42-5; *trans*-$PtCl_2$(ethylene)(pyridine), 12078-66-9; poly(isobutylene), 9003-27-4.

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