Adsorption and Desorption of Chemical Warfare Agent Simulants on Silica Surfaces with Hydrophobic Coating

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Aim of our study is finding adsorbents suitable for pre-concentration of chemical warfare agents (CWAs). We considered Tenax, bare silica and polydimethylsiloxane (PDMS)-coated silica as adsorbents for dimethyl methylphosphonate (DMMP) and dipropylene glycol methyl ether (DPGME). Tenax showed lower thermal stability, and therefore, desorption of CWA simulants and decomposition of Tenax took place simultaneously. Silica-based adsorbents showed higher thermal stabilities than Tenax. A drawback of silica was that adsorption of CWA simulant (DMMP) was significantly reduced by pre-treatment of the adsorbents with humid air. In the case of PDMS-coated silica, influence of humidity for CWA simulant adsorption was less pronounced due to the hydrophobic nature of PDMS-coating. We propose that PDMS-coated silica can be of potential importance as adsorbent of CWAs for their pre-concentration, which can facilitate detection of these CWAs.

Key Words : Chemical warfare agents (CWAs), Pre-concentration, Polydimethylsiloxane (PDMS)-coating, Silica

Introduction

Detection of ultralow concentration of chemical warfare agents (CWAs) has been attracting attention recently in defense development. CWAs with high vapor pressure can be easily spread out in the atmosphere, and therefore, detection of low-concentration of CWAs can allow initiation of protection process from CWAs as early as possible, ultimately hindering diffusion of CWAs into a wider area.

For detection of CWAs, ion mobility spectroscopy, gas chromatography and mass spectrometry can be used. Lowering detection limit of these instruments is an important issue; on the other hand, pre-concentration of CWAs for detection can be an economic and efficient way of increasing detection limit of conventional detectors for CWAs. Pre-concentrators can include highly efficient adsorbents for CWAs and heating unit. Increasing temperature of the adsorbents will result in desorption of CWAs adsorbed (or accumulated) on adsorbent surface, which can temporarly increase local concentration of CWAs in the pre-concentration-unit, and enhance the detection limit of detector by many orders of magnitude.

In the present work, we studied adsorption and desorption of CWA simulants on Tenax, and bare and PDMS-coated silica. Note that Tenax is a brand name of poly(2,6-diphenylphenylene oxide), which is a porous polymer. We show that oxide-based porous materials with hydrophobic coating can be good candidates for adsorbents of CWAs for pre-concentration.

Experimental

For evaluating pre-concentration ability of adsorbents for CWA stimulants, two adsorbent samples were prepared, which are bare-, and polydimethylsiloxane (PDMS)-coated silica. In addition to silica-based materials, Tenax was also tested as adsorbent of CWAs. Tenax is a porous polymer, which is widely used as adsorbent of organic molecules.

The PDMS-coating process is summarized in Figure 1. Before PDMS-coating, bare silica (Sigma Aldrich, Davisol® grade 646, pore size 15 nm, grain size 250-500 µm) was outgassed at 500 °C for 3 h under atmospheric conditions to remove impurities. Then 9 g of purified silica and 3 g of cured PDMS blocks (Dow Corning, Sylgard 184, the weight ratio of Sylgard 184 to curing agent was 10:1, and size of each PDMS-clock was 1 cm³) were placed in 3-neck round bottom flask with magnetic stirring bar. The flask temperature was maintained at 150 °C for an hour which was controlled by temperature control system consisting of heating mantle, k-type thermocouple, temperature controller and power supply. During this process, vaporized PDMS formed thin hydrophobic film on the surface of silica. Details of structures and properties of PDMS-coated surfaces of diverse nanomaterials can be found elsewhere.

Brunauer-Emmett-Teller (BET) surface area of bare and
Results and Discussion

In order to shed light on adsorption and desorption behaviors of CWA simulants on various adsorbents, TPD studies were carried out. DMMP was used as first CWA stimulant.

Figure 3 shows GC spectra collected during the Tenax adsorbent exposed to DMMP was subsequently heated at 360 °C. Not only molecular desorption of DMMP but also decomposition product of Tenax adsorbent can be identified at the same temperature, i.e. before desorption of DMMP was completed, the adsorbent decomposition was initiated. After heating the sample above 360 °C for long time, the originally beige Tenax became black, and our quartz reactor was heavily contaminated by the decomposition products of Tenax. This result implies that thermal stability of Tenax, porous polymer, is not sufficiently high as adsorbent of pre-concentration device for detector of CWAs. Once Tenax is used as adsorbent for pre-concentration of CWAs, the following should be considered.

Temperatures below the decomposition temperature of adsorbents should be used for pre-concentration process, since decomposition product of polymer-based adsorbents can contaminate detecting instruments such as GC. On the other hand, when sufficiently high temperature is not reached during desorption process, the desorption rate, which can be one of determining factors of pre-concentration efficiency, will be very low.

Adsorbents should be replaced after every pre-concentration process of CWAs consisting of exposure of adsorbent to the atmosphere for a certain period of time and subsequent heating, since each pre-concentration process will destroy adsorbent structure, and the pre-concentration ability of the used adsorbent will be different from that of the original adsorbent. Considering that Tenax and other polymer-based porous adsorbents are relatively expensive, it is necessary to find novel adsorbents, which are thermally more stable and less expensive.

Porous oxide-based materials, particularly silica, can be one of the potential adsorbents for pre-concentration of CWAs, since they are thermally stable and more economic. A problem of using oxide-based materials is that their surfaces often show hydrophilicity and therefore, water adsorption can be preferred to the adsorption of CWAs, which can lower the pre-concentration efficiency under highly humid conditions due to the competitive character of water and adsorbed CWAs.

Figure 3. GC spectrum taken while the DMMP-covered Tenax was heated to 360 °C.
CWA adsorption.\textsuperscript{11,12} In order to solve this problem, hydrophobic thin film was deposited on silica. Table 1 shows surface areas and pore volumes of bare and PDMS-coated silica samples, which were determined using BET method and BJH analysis. Both samples showed quite analogous surface areas and pore volumes, indicating that PDMS at least did not fill the pore of silica. Even though surface area and pore volume did not show much change after PDMS–coating, hydrophilic surface property disappeared after PDMS–coating, indicating that PDMS thin film actually formed on top of silica surface: the water contact angle of PDMS-coated silica dispersed on top of epoxy glue on slide glass turned out to be higher than 130°, and this value is close to water contact angle of lotus leaves in nature (Fig. 4).

TPD data taken after DMMP adsorption on bare and PDMS-coated silica under different conditions are shown in Figures 5 and 6. For bare silica exposed to DMMP vapor without treatment of humid atmosphere, TPD spectrum showed two broad states centered at 250 and 400 °C, respectively (Fig. 5). These peaks can be tentatively assigned to physically adsorbed DMMP (multilayer of DMMP inside pore) and chemically adsorbed ones intact to the silica surface, respectively (Fig. 5). When the bare silica was pre-treated with humid atmosphere before DMMP exposure, a significant reduction of the TPD peak area was found, indicating that water adsorption inhibited DMMP adsorption. The lower-temperature peak corresponding to the physically adsorbed DMMP inside pore disappeared after humid air pre-treatment, indicating that water molecules were trapped inside pore, and protected further adsorption of DMMP. It is notable that the desorption temperature of DMMP is significantly higher than that of typical environmental pollutant such as toluene.\textsuperscript{13,14}

In the case of PDMS-coated silica, exposure to DMMP without treatment under humid air resulted in appearance of desorption states between 200-400 °C. It is notable that PDMS-coating resulted in a significant reduction in the TPD peak area with respect to the corresponding spectrum of bare silica. When the PDMS-coated silica was pre-treated with humid air and then exposed to DMMP, decrease in the amount of DMMP adsorption by water was found; however, the influence of humidity for adsorption capacity of PDMS-coated silica was less pronounced comparing to the case of bare silica (Table 2). It is notable that the higher-temperature desorption peak of DMMP from PDMS-coated silica was

<table>
<thead>
<tr>
<th>Sample</th>
<th>Without H\textsubscript{2}O exposing (mmol)</th>
<th>With H\textsubscript{2}O exposing (mmol)</th>
<th>Reduced amount (%)\textsuperscript{a}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bare-SiO\textsubscript{2}</td>
<td>233.3</td>
<td>54.3</td>
<td>76.7%</td>
</tr>
<tr>
<td>PDMS-SiO\textsubscript{2}</td>
<td>155.2</td>
<td>103.2</td>
<td>33.5%</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Reduced amount (%) = \frac{A_{\text{w/o}} - A_{\text{with}}}{A_{\text{w/o}}} \times 100

\(A_{\text{w/o}}\) – Desorbed DMMP amount from the sample without H\textsubscript{2}O exposure

\(A_{\text{with}}\) – Desorbed DMMP amount from the H\textsubscript{2}O exposed sample

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**Table 1.** BET surface area and pore volume of bare SiO\textsubscript{2} and PDMS coated SiO\textsubscript{2}.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Surface area (m\textsuperscript{2}g\textsuperscript{-1})</th>
<th>Pore volume (cm\textsuperscript{3}g\textsuperscript{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bare-SiO\textsubscript{2}</td>
<td>306.24</td>
<td>1.1283</td>
</tr>
<tr>
<td>PDMS/SiO\textsubscript{2}</td>
<td>310.92</td>
<td>1.3074</td>
</tr>
</tbody>
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**Figure 4.** Water contact angles of surfaces consisting of bare and PDMS-coated silica.

**Figure 5.** TPD spectra of DMMP desorbed from bare silica with and without humid air pre-treatment.

**Figure 6.** TPD spectra of DMMP desorbed from PDMS-coated silica with and without humid air pre-treatment.
shifted to even higher temperature upon humid air pre-treatment (Fig. 6). Humid air seems to have slightly modified the structure of PDMS-coated silica, thereby increasing desorption energy of chemisorbed DMMP on PDMD-coated silica. Further studies are required for shedding light on this issue.

Figure 7 shows GC spectra taken during bare and PDMS-coated silica exposed to DPGME, another CWA simulant used in the present work, were heated to 300 °C. It is notable that not a single peak corresponding to molecular desorption of DPGME, but also many peaks from fragmentation of DPGME during heating and desorption can be observed. When the sample was heated to 630 °C, still residue of adsorbed DPGME was remained on the surface of adsorbents, and the originally white particles turned into black after TPD experiments (Fig. 8). It is also worth mentioning that hydrophobicity of PDMS-coated silica disappeared after heating at 630 °C.

Overall, one can suggest the following for constructing pre-concentration device of CWAs based on adsorption of CWAs on adsorbents and desorption of CWAs by heat-treatment of adsorbents.

i) Oxide-based materials with hydrophobic coating exhibit much higher thermal stability than porous polymers. Due to many problems aforementioned, which can be caused by use of thermally less stable polymer-based adsorbents, other materials than polymers should be considered as adsorbents and oxide-based porous materials with hydrophobic coating can be good alternatives.

ii) For some CWAs such as DPGME, fragmented species can be detected during desorption taking place. Fragmented species can also be used for detecting CWAs. Moreover, fragmentation patterns during heating adsorbents can also be used as fingerprint for qualitatively identifying CWAs. Fragmentation pattern of a molecule in mass spectrometry has been widely used for qualitative identification of an unknown molecule, and similar technique can be developed and used based on TPD technique.

iii) Some CWAs can be completely molecularly desorbed from adsorbents, whereas some others can be fragmented on the surface during heating, leaving surface residues after thermal treatment. Such adsorbents cannot be repeatedly used for pre-concentration of CWAs, since pre-concentration efficiency using such adsorbent will change by repeated use of the adsorbents. One should use fresh unused adsorbents for every new pre-concentration process; in this respect, exploration of less expensive adsorbents for pre-concentration of CWAs is required. We suggest that porous silica with hydrophobic coating could be suitable for this purpose.

Conclusion

Adsorption and desorption of various CWAs (DMMP and DPGME) on bare and PDMS-coated silica were studied using TPD with and without pre-treatment under humid atmosphere. Bare silica showed higher adsorption capacity of DMMP than that of PDMS-coated silica. However, adsorption of DMMP on bare silica was significantly reduced by pre-treatment of the adsorbents with humid air. In the case of PDMS-coated silica, influence of humidity for DMMP adsorption was less pronounced due to the hydrophobic nature of PDMS-coating. For DPGME, not only molecular desorption but also desorption of fragmented species were observed. We propose that PDMS-coated silica can be one of the most promising candidates for CWAs pre-concentration adsorbent, which can facilities detection of these CWAs.

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References