



이학박사 학위논문

Study of Volatile Organic Compounds Adsorption on Porous Inorganic Materials by Surface Modification

표면 조작을 통한 다공성 무기재료의 휘발성유기화합물 흡착에 관한 연구

2023년 2월

서울대학교 대학원

화학부 무기화학 전공

심인근

Study of Volatile Organic Compounds Adsorption on Porous Inorganic Materials by Surface Modification

지도 교수 손 병 혁

이 논문을 이학박사 학위논문으로 제출함 2023년 2월

> 서울대학교 대학원 화학부 무기화학 전공 심 인 근

심인근의 이학박사 학위논문을 인준함 2023년 2월



Abstract

Study of Volatile Organic Compounds Adsorption on Porous Inorganic Materials by Surface Modification

In-Keun Shim Department of Chemistry, Inorganic Chemistry The Graduate School Seoul National University

Nanotechnology has the potential to revolutionize a wide range of fields, including electronics, energy, medicine, environment, and materials science. The unique properties of nanostructures, such as their high specific surface area and tunability, make them particularly useful for various applications in nanotechnology. With rapid advancements in nanotechnology, the interest of people moves from the convenience of nanotechnology to the health concerns such as the quality of breathing air, the cleanliness of drinking water, and the safety of foods. Among them, the indoor air quality has got the most attention since the beginning of the COVID-19 pandemic. To date, a lot of adsorbents for air and water purification by utilizing the nanomaterials such as activated carbon, carbon nanotube, boron nitride,

i

cellulose nanocrystals, cellulose nanofibrils, layered double hydroxide, graphene, porous silica, metal-organic framework, and so on.

In this dissertation, porous silica nanoparticles and graphene nanomaterials are mainly investigated as proposed effective adsorbents for removing toxic chemicals in indoor air. Unlike the method for evaluating the removal of pollutants in water, the assessment of pollutants removal performance in the air tends to show a high coefficient of variation (CV) due to the intrinsic nature of the matrix. To reduce this uncertainty, the standard methods published by the international organization for standardization (ISO) were applied in this study from the specimen preparation to quantitative analysis.

In chapter 1, the research background for indoor air pollutants, adsorbents, mesoporous silica nanoparticles, graphene oxide nanomaterials is briefly described.

In chapter 2, among the previously reported various types of porous silica, a mesoporous silica nanoparticles with wrinkle structure was investigated as a adsorbent for indoor benzene, toluene, ethylbenzene, and xylene (BTEX). Although the template-directed mesoporous silicas using surfactants have been widely studied for the past decades, poor accessibility to their active sites inside pores has limited their practical applications. From the structural point of view, the proposed silica is expected to enhance the accessibility of functional materials inside their pores. In addition, the mesoporous dimensions and the size of the silica could be easily controlled by handling the adding amount of n-butanol in preparation

ii

process. The BTEX removal ability with surface modified mesoporous silica is looked into from the physisorption point of view. The proposed silica nanomaterials show over 90% of BTEX removal performance except for benzene.

In chapter 3, 3D structured graphene oxide and n-doped graphene oxide are designed to increase the number of active sites for formaldehyde adsorption in air. To embody the 3D structure to graphene oxide, the innate feature of self stacking between single graphene layers is physically prevented and expanded porosity in materials is expected to increase the adsorption capacity. The influences of adsorption performance by adopting doping elements on graphene oxide sheets and regulating relative humidity are focused on this chapter from the chemisorption point of view. Although there is a difference depending on the relative humidity, n-doped mesoporous graphene oxides show the removal performance of formaldehyde in air in a range of 85.8-44.3%.

In chapter 4, the status of indoor air pollutants in Korea is discussed and their risk assessments results are estimated. The sick building syndrome symptoms of workers in underground shopping shops is investigated with the concentration of indoor air pollutants. The concentrations of n-butanol, n-heptane, and xylene were associated with eye irritation symptoms, while those of n-heptane were associated with respiratory symptoms, and those of benzene, n-heptane, and decanal were associated with general symptoms. In part 2, the representative indoor air pollutants (e.g., single VOCs, TVOCs,

iii

carbonyl compounds, carbon dioxide, PM10, and PM2.5) monitoring results in three different types of housing (apartment, detached houses, and multiplex houses) were discussed. The statistical factor analysis was conducted to find influencing factors on the levels of pollutants. For example, the concentration of formaldehyde in apartments and detached houses were highly influenced by interior building materials.

Keywords : porous material, adsorption, surface modification, air pollutants, silica, graphene, VOCs *Student Number* : 2012-30876

Table of Contents

Abstract ·····	i
Table of Contents	····· vi
List of Figures	······ix
List of Tables	······ xiv
List of Schemes	······ xviii

Chapter 1. General Research Background1
1. Indoor air and related physical-chemical technologies
2. Adsorption and adsorbents
3. Mesoporous silica materials
4. Graphene oxide materials14
5. References 20
Chapter 2. Surface-Modified Wrinkled Mesoporous Silica as

an Effective Adsorbent for Benzene, Toluene, Ethylbenzene, and Xylene in Indoor Air ······ 25 1. Introduction 27 2. Experimental 30 3. Results and Discussion 34 4. Conclusions 56

1.	Introduction ·····	63
2.	Materials and Methods	65
3.	Results and Discussion	70
4.	Conclusions	83
5.	References ·····	84

Chapter 4. Indoor Air Pollutants and Their Risk Assessments

1.	Introduction 91
2.	Materials and Methods
3.	Results ····· 99
4.	Discussion
5.	Conclusions 113
6.	References

1.	Introduction	121
2.	Materials and Methods	123
3.	Results and Discussion	127
4.	Conclusions	141
5.	References ·····	141

Appendix

brication of Wrinkled Silica Nanoparticles for VOC	Cs
atement in air ······ 145	5
Introduction	7
Experimental ······ 149)
Results and Discussion	l
Conclusions	1
References ······ 155	5

Abstract	in	Korean ·····	15	57	1
----------	----	--------------	----	----	---

List of Figures

Chapter 1

Figure	1.	Main sources of indoor air pollutants
Figure	2.	(a) Factors affecting the adsorption capacity of VOCs and
		formaldehyde, (b) example of VOC abatement mechanism
		by biochar
Figure	3.	General synthesis method for mesoporous silica using a
		surfactant-templated route 11
Figure	4.	TEM images of various mesoporous silica nanoparticles (a)
		hollow silica, (b) wrinked mesoporous silica, (c) SBA-15,
		(d) MCM-41, (e) hollow silica nanocapsules, (f) hollow
		silica nanocubes. 13
Figure	5.	Several representative mesoporous silicas and their space
		groups 14
Figure	6.	Schematic representation of (a) ideal structure of AB
		stacked graphite, (b) structure of a graphene sheet with
		zig-zag and arm chair edges, and (c) HRTEM image of C-C
		bond at the arm chair edge in graphene 15

Figure 7. Schematic synthetic procedure of graphene oxide by

Chapter 2

- Figure 3. Thermogravimetric analysis curves of as-prepared WSNs, SE-WSNs, OTES-WSNs, HDTMS-WSNs, and TEPS-WSNs.
- Figure 4. N₂ adsorption-desorption isotherms of the as-prepared WSNs, SE-WSNs, OTES-WSNs, HDTMS-WSNs, and TEPS-WSNs.
- Figure 5. (a) BJH pore size distribution of WSNs, SE-WSNs, OTES-WSNs, HDTMS-WSNs, and TEPS-WSNs. (b)
 Schematic of the rationale for the difference in pore size distributions between WSNs modified with different organosilanes. 43

- Figure 6. (a) Adsorption capacities of SE-WSNs, OTES-WSNs, HDTMS-WSNs, and TEPS-WSNs for BTEX and (b) schematic illustration for their adsorption properties. 50
- Figure 7. The recyclability profiles of various WSNs. 55

Chapter 3

Figure	1.	The schematic diagram (a) and instrument system picture
		(b) of formaldehyde adsorption test
Figure	2.	FE-SEM images for (a, b) MGs and (c, d) NMGs 71
Figure	3.	Powder X-ray diffraction patterns for (a) GO (b) MGs (c)
		NMGs 72
Figure	4.	(a) Nitrogen adsorption-desorption isotherms and (b) BJH
		pore size distribution of MGs and NMGs77
Figure	5.	FE-SEM images and EDS maps of NMGs78
Figure	6.	(a) XPS survey specra of MGs and NMGs (b)
		high-resolution N 1s spectra of NMGs79
Figure	7.	Adsorption capacity of MGs and NMGs for formaldehyde in
		air 80

Chapter 4 Part I

- Figure 1. Prevalence of sick building syndrome (SBS) symptoms in underground shopping district store workers (n=128). · 100
- Figure 3. Associations (aOR with 95% CI) between SBS symptom groups, aldehyde compounds and VOC concentrations (per μg m⁻³). Demographic and job characteristic variables identified in the univariate analysis, sex, and age were included, and environmental variables (i.e., CO₂, temperature, and relative humidity) selected using stepwise methods were included in the multiple logistic regression model. 107

Chapter 4 Part Ⅱ

Figure 1. Seasonal variation of indoor air pollutants in studied houses.

Appendix

Appendix/Figure	1.	(a) Coupling agents for surface modification, (b)
		Schematic procedure for preparing surface
		modified WSNs

- Appendix/Figure 2. (a) WSNs packed thermal desorption glass tubes, (b) diagram of common thermal desorption tube. 151
- Appendix/Figure 4. Adsorption capacities of WSNs for (a) aliphatic hydrocarbons, (b) aromatic hydrocarbons, (c) aldehyde, alcohol, and acetate, (d) ketone and terpene. 154

List of Tables

Chapter 1

Table	1.	Physical/Chemical	Technologies	for	Removal	of	VOCs	and
		Formaldehyde		•••••		•••••	•••••	6

Table 2. Comparisons between Physisorption and Chemisorption. 8

```
Table 3. Representative Methods for Preparing Graphene Oxide. ... 17
```

Chapter 2

Table 1. Structural Properties of the Wrinkled Silica Nanoparticles.4	Table 1	1. S [·]	tructural	Properties	of	the	Wrinkled	Silica	Nanopartic	les.4
--	---------	-------------------	-----------	------------	----	-----	----------	--------	------------	-------

- **Table 2.** Estimated Interaction Energy (ΔE_{int}) Values for SeveralBenzene-Hydrocarbon Clusters.48
- Table 3. The Summary of Recent Works and WSNs Adsorbents Used

 in This Study.

 52

Chapter 3

Table 1.	Comparison of Structural Parameters of GO, MGs, and
	NMGs Resulting from the XRD Patterns75
Table 2.	Comparison of Pore Structure Parameters of MGs and

- NMGs. ----- 76
- Table 3. Density Functional Theory (DFT) Calculation Results

 between N-Doping Graphene and Formaldehyde.

 81
- Table 4. Estimated Adsorption Energy of NMGs for FormaldehydeCombining the Results from the DFT Calculation andHigh-Resolution N 1s XPS Spectra.82

Chapter 4 Part I

Table	1.	Thermal Desorption Gas Chromatography/Mass Spectrometry
		(TD-GC/MS) Analytical Conditions
Table	2.	Prevalence of SBS Symptoms in Underground Shopping
		District Store Workers. 99
Table	3.	Distribution of SBS Symptom Prevalence by Demographic
		and Job Characteristics 101
Table	4.	Correlations among Perceived Indoor Air Quality Index. 103
Table	5.	Indoor Aldehyde Compounds, VOC Concentrations ($\mu g m^{-3}$),

 Table 6. Relationships between SBS Symptom Groups and

 Environmental Monitoring Data.

 108

Chapter 4 Part Ⅱ

Table 1	1.	House Characteristics. 124
Table 2	2.	Comparison of Indoor Air Pollutant Concentrations in
		Different Housing Types. 128
Table 3	3.	Indoor to Outdoor Ratios of the Concentration of Indoor Air
		Pollutants in Apartment, Detached houses and Multiplex
		Houses
Table 4	4.	Association between Indoor Pollutants Levels and Interior
		Renovations. 134
Table 5	5.	Association between Indoor Pollutants Levels and Length of
		Residence. 136
Table (6.	Association between Indoor Pollutants Levels and Floor. 138

Appendix

Appendix/Table 1. Frequently Detected VOCs in Indoor Air and Their

Properties. 148

List of Schemes

Chapter 2

Scheme 1. Schematic of the (a) Fabrication of Wrinkle-Structured Silica Nanoparticles and (b) Standard BTEX Adsorption Test Method Based on the International Standard ISO 16017-1:2000 Using the Materials Fabricated in This Study.

Chapter 3

Chapter 1.

General Research Background

1. Indoor air and related physical-chemical technologies

There are thousands of pollutants indoors, and it is known that about 250 of them affect our health.^[1] For that reason, the US Environmental Protection Agency (US EPA) points out indoor air pollution as one of the five most urgent environmental problems facing the United States,^[2] and the WHO reports that the number of deaths due to indoor air pollution reaches up to 3.2 million per year in 2020.^[3] According to the US EPA, the level of pollutant inside building can be significantly higher than those found outdoors, sometimes even more than 100 times higher. This could be due to a variety of factors, such as inadequate ventilation, airtight building design for saving energy, the presence of source of pollution indoors, and the accumulation of pollutants over time. Indoor pollutants stem from outdoor-indoor transfers or specific indoor sources. Most indoor pollutants derive from anthropogenic activity (e.g., remodeling/repair, cleaning, cooking, combustion processes) and building materials as shown in Figure 1.



Figure 1. Main sources of indoor air pollutants.

Among the thousands of indoor pollutants, the most important ones are particulate matter (e.g., total suspended particulate(TSP), PM10, and PM2.5) and volatile organic compounds in terms of relating to human health.

Volatile organic compounds (VOCs) is defined as organic compounds whose boiling point is in the range from (50 °C to 100 °C) to (240 °C to 260 °C) in International Organization for Standardization (ISO).^[4] Among them, four chemicals so called BTEX (benzene, toluene, ethylbenzene, and xylene) is the most noticeable pollutants due to their ubiquitous and toxic characteristics. Benzene has been classified as carcinogenic to humans by the International Agency for Research on Cancer (IARC) since 1979. The carpets, paints, plastics, furniture, environmental tobacco smoke (ETS) and polymeric furnishing are major indoor sources of benzene.^[5] The highest concentration of benzene has been monitored in shopping shops (2.5-48 µg m⁻³) followed by offices (1.4-5.5 μ g m⁻³), homes (0.7-4.4 μ g m⁻³) and schools $(0.5-3 \ \mu g \ m^{-3})$.^[6-8] Toluene is not a confirmed carcinogenic chemicals, but it is one of the most common indoor air pollutants and the most abundant among BTEX. It is released from a variety of household products including adhesives, coatings, and cosmetics combustion devices.^[9] Shopping complexes present the highest toluene levels (15-164 μ g m⁻³), followed by office (6-32 µg m⁻³), and houses (3-20 µg m⁻³). Ethylbenzene is used as a solvent during manufacturing of plastics, paints, adhesives, and other building materials. It has been classified as a potential human carcinogen by IARC and recorded their concentration in a range from 0.8 to

16 µg m⁻³ in shopping centers and homes.^[8] Xylene is slightly greasy liquid of great industrial value and has three structural isomers: ortho, meta, and para. Indoor sources of xylene are dyes, polymers, cleaning products, pharmaceuticals, and paints. It is detected in a range of concentration from 0.3 to 16 µg m⁻³ in houses and schools.^[8] Xylene is a suspected carcinogens associated with an increased risk of leukemia, non-Hodgkin's lymphoma and colon/rectum cancer.^[10] Formaldehyde is known a genotoxic chemical and classified as a human carcinogen by IARC. It is mainly emitted from wood-based products assembled using urea-formaldehyde resin but can also be produced by paints, cigarette smoking, insulation forms, electronics, fabrics or the use of vanishes and floor finishes. And formaldehyde is also generated by oxidation of other VOCs with ozone or radiation indoors.^[11] The concentration of exposure in houses and offices is in a range from 7.7 to 30 µg m^{-3.[8]} It is hard to reduce or eliminate these indoor air pollutants in a cost-effective or technically feasible manner, and active abatement units can be installed to lower their levels. These devices were traditionally made up of physical-chemical technologies such as filters and ozonizers, which were part of a central heating and ventilation system or used as portable units. Currently, the market for physical/chemical technologies for indoor air treatment is dominated by mechanical and electronic filtration, adsorption, and ozonation. Among them, adsorption and photocatalytic oxidation methods have been widely adopted in practice especially for abatement of VOCs and formaldehyde as shown in Table 1.

Table 1. Physical/Chemical Technologies for Removal of VOCs and

Formaldehyde.

Design	Air flow (m ³ /h)	Removal capacity (µg/m ² ·h)	Single pass efficiency (%)	Reference
Adsorption				
Indoor passive panels (gypsum based) - Dimensions: 0.089 m ²	0.2	FA: 40-140 T: 30-210	-	[12]
Granular activated carbon - 7 g of adsorbent	0.06	-	B: 81.5-91.6 T: 86.6-100 E: 91.6-99.2 X: 89.9-100	[13]
Porous ferrihydrite / SiO_2 composite	-	FA: 6.3-8.1 mg/g	-	[14]
High-grade activated carbon filter (portable)	510	-	FA: 0.6 T: 32.0	[15]
Activated carbon prefilter	569	-	FA: 0.2, T: 7.8	[15]
Non-woven polyester filter impregnated with activated carbon (portable)	340	-	FA: 1.5 T: 26.0	[15]
Granular activated carbon + KMnO4-impregnated alumina (in-duct)	-	-	FA: 1.4 T: 3.5	[15]
Photocatalytic oxidation				
$\begin{tabular}{lllllllllllllllllllllllllllllllllll$	0.2	T: (a) 59-120 (b) 58-70 (c) <15	-	[12]
UV light (253.7 nm) TiO ₂ converter + MERV11 filter (in-duct)	720	-	B: 0.58, T: 0.58 E: 0.50, X: 0.32 FA: 0.08	[16]
ZnO nanorod-wrapped PTFE nanofiber antibacterial membrane with Ag nanoparticles (7.07 cm ² , 0.1 mm thick)	-	-	FA: 60	[17]
Hybrid method				
$\overline{\text{ZIF8-SiO}_2} \text{ nanofiber composite membrane} \\ \text{- Dimensions: 7.07 cm}^2$	0.013	FA: 36.04	FA: 80	[18]
Dielectric barrier discharge NTP + UV light + SiO ₂ /TiO ₂ -coated glass fiber tissue (6.5 g/m ² SiO ₂ + 6.5 g/m ² TiO ₂)	2	-	B: 58-90	[19]
MOF TiO ₂ /UiO-66-NH ₂ composites + UV light	0.06	T: 106.7 mg/g	T: 47.2	[20]

* (abbreviation) FA: formaldehyde, B: benzene, T: toluene, E: ethylbenzene, X: xylene

2. Adsorption and adsorbents

Most chemical, physical, and biological processes arise at the boundary between two phases. Adsorption is a process in which atoms, ions, or molecules from a gas, liquid, or dissolved solid adhere to a surface. This process generates a film of the adsorbate on the surface of the adsorbent.

In a rule, the adsorption process is generally classified as physisorption (characteristic of weak van der Waals forces) or chemisorption (characteristic of covalent bonding). They are similar in many ways, but there are some important differences between the two. In chemisorption, the adsorbed species forms a chemical bond with the surface, whereas in physisorption, the attraction between the adsorbate and the surface is primarily due to van der Waals forces, which are weak, non-covalent interactions. One way to distinguish between chemisorption and physisorption is by looking at the strength of the interaction between the adsorbate and the surface. Chemisorption is typically a much stronger interaction than physisorption, and as a result, chemisorbed species are much harder to remove from the surface. This can be observed experimentally by looking at the amount of energy required to desorb the adsorbed species. Another way to distinguish between the two types of adsorption is by looking at the coverage of the adsorbed species on the surface. In chemisorption, the coverage is typically low, with only a small number of adsorbed species per unit area of the surface. In contrast, in physisorption, the coverage can be much higher, with a large number of adsorbed species per unit area. Overall, the main

7

difference between chemisorption and physisorption is the strength of the interaction between the adsorbate and the surface. Chemisorption involves a chemical bond, whereas physisorption is a weaker van der Waals interaction. This difference in interaction strength leads to differences in the amount of energy required for desorption and the coverage of the adsorbed species on the surface.

	Physisorption	Chemisorption
Force	Van der Waals	Chemical bonds
Pathway	Reversible	Irreversible
Favor condition	Low temperature	High temperature
Target	Non-specific	Relatively specific in nature
Forming layer	Multi-molecular layer	Monolayer
Activation energy	Low	High
Adsorption enthalpy	Low (20-40 kJ mol ⁻¹)	High (80-240 kJ mol ⁻¹)

Table 2. Comparisons between Physisorption and Chemisorption.

In an environmental aspect, adsorption is a process in which pollutants are captured on the surface of adsorbent materials like activated carbon and zeolites. These materials can be used in construction materials and are easy to integrate into indoor environments. However, their efficiency can be reduced by high humidity and variable pollutant levels. The specificity of adsorbent materials for certain pollutants could also limited their ability to remove other pollutants. To maintain their efficiency and prevent re-emission of pollutants, adsorbent materials may need to be replaced or regenerated. The efficiency of adsorption devices for removing VOCs could vary greatly and depends on the several factors as described in Figure 2. Up to now, carbon based materials (e.g., activated carbons, biochar, carbon nanotubes, graphenes) and silicon based materials (e.g., MCM-41, zeolites, porous silicas), and metal organic frameworks (MOFs) are well known for high removal capacities against for formaldehyde and BTEX.

Ozonization and photocatalytic oxidation methods are also useful as mentioned before, but these methods using ozone or photocatalysts are partially dissatisfied and unsuitable to apply in indoor air due to the possibility to generate toxic side products when decomposing VOCs and toxicity of ozone itself. Thus, the demand of developing efficient adsorbents is highly requested nowadays. Overall, adsorption could be considered the best way in physical/chemical technology for removing indoor VOCs and formaldehyde.



Figure 2. (a) Factors affecting the adsorption capacity of VOCs and formaldehyde, (b) example of VOC abatement mechanism by biochar.^[21]

3. Mesoporous silica materials

According to International Union of Pure and Applied Chemistry (IUPAC) nomenclature, mesoporous material is a type of porous material that has pores with diameters ranging from 2 to 50 nm.

Mesoporous silica, a type of nanoporous material with hexagonal pores of size 2-3 nm, was first synthesized by the Mobile Corporation in 1990 and was named MCM-41.^[22] This was the first instance of using a cationic surfactant, specifically cetyl ammonium bromide (CTAB), as a template to create pores in a silica framework. Since then, various types of surfactants including cationic, and neutral have been used to synthesize silica nanoporous materials.

Mesoporous silica is often made through a process called sol-gel chemistry in an aqueous solution. This process involves preparation of an inorganic polymer network at low temperatures using hydrolysis and condensation of a silica precursor (Si(OEt)₄), such as tetraethyl orthosilicate (TEOS). In hydrolysis, the alkoxide group (OR) of the silica precursor is replaced by the silanol group (Si-OH) by the nucleophilic attack of the oxygen atom of the water. And dimers, linear trimer, cyclic and polymeric species with siloxane bonds (Si-O-Si) are formed by condensation reactions. To get mesoporous materials, surfactants such as cetyltrimethylammonium bromide (CTAB) are used. These surfactants tend to form micelles at concentrations above their critical micelle concentration (CMC), and the silica precursor could then condense on the surface of the micelles to form

10

silica particles. Surfactants play a key role in determining the pore size and pore volume of silica materials.

There are many different types of surfactants available and the advance in sol-gel chemistry, which has allowed for the development of various types of mesoporous silica with different structures. By using them, the particle size, morphology, and pore structure of mesoporous silica could be intentionally designed and their synthesis process could be easily controlled. The template surfactant could be removed through calcination or solvent extraction to create pores as a final step in this process (Figure 3).



Figure 3. General synthesis method for mesoporous silica using a surfactant-templated route.^[22]

Silica-based mesoporous matrices have the following unique structural properties: 1) an ordered porous structure; 2) a large pore volume and surface area, providing high potential for efficient molecule adsorption; 3) a tunable particle size ranging from 50 to 300 nm; 4) an easy of surface functionalization. The common chemicals used for surface modification are silanes and these are grafted on silica surfaces by condensation reaction between hydroxyl group of surface and chloro, epoxy, alkoxy groups in silane coupling agents. Typical silylation is accomplished by one of the following procedures.

$$\equiv Si - OH + Cl - SiR_3 \xrightarrow{base, 25^{\circ}C} \equiv Si - OSiR_3 + HCl \cdot base$$
(1)

$$\equiv Si - OH + R'O - SiR_3 \xrightarrow{100^\circ \mathbb{C}} \equiv Si - OSiR_3 + HOR'$$
⁽²⁾

$$2 \equiv Si - OH + HN(SiR_3)_2 \xrightarrow{25^\circ C} 2 \equiv Si - OSiR_3 + NH_3$$
(3)

By imparting various functionality on the surface, the applicability of mesoporous silicas could be further broadened.

Figure 4 shows the various morphologies of typical mesoporous silica nanoparticles. After the discovery of MCM-41, researchers began developing different types of silica materials with different pore sizes and shapes. In 1998, Stucky and colleagues reported the synthesis of SBA-15 using a triblock copolymer called P123. This discovery was a significant step forward in the design of porous silica nanomaterials, because it allowed

researchers to control the size of the pores. Since then, many different methods have been reported for synthesizing pore-extended SBA-15 with pore sizes ranging from 5 to 30 nanometers using various combinations of surfactants and swelling agents. These methods have been used to synthesize a wide range of silica materials with different structures, including hollow spheres, wrinkled silica materials, spherical materials with hexagonal pores, rod-shaped materials, silica nanocapsules, and hollow silica nanocubes.



Figure 4. TEM images of various mesoporous silica nanoparticles (a) hollow silica,^[24] (b) wrinked mesoporous silica,^[25] (c) SBA-15,^[26] (d) MCM-41,^[27] (e) hollow silica nanocapsules,^[28] (f) hollow silica nanocubes.^[29]


Figure 5. Several representative mesoporous silicas and their space groups.^[30]

Mesoporous silica nanomaterials could be classified by means of their pore structures as shown in Figure 5.^[30] Silica nanomaterials with different shapes and sizes have been studied extensively for many different applications because of their attractive structural properties, low toxicity, and good biocompatibility. Mesoporous silica has been explored for a wide range of purposes, including drug delivery,^[31] adsorption and separation,^[32] CO₂ gas capture,^[33] biochemistry,^[34] gene delivery,^[35] food science,^[36] DNA delivery,^[37] and as a support for heterogeneous catalysts.^[38]

4. Graphene oxide materials

Graphite is a form of carbon that could occur naturally or be produced

artificially. Their individual sp² carbon layers could be stacked either be in a hexagonal (AB) or rhombohedral (ABC) pattern, or the stacking could be irregular (turbostratic) as shown in Figure 6(a).^[39] Generally, natural graphite is used as a starting material to preparation of graphene or graphene oxide.

Graphene is an allotrope of carbon made up of a single layer of atoms arranged in a repeating hexagonal lattice nanostructure as shown in Figure 6 (b). Due to its innate properties, graphene surpasses all other carbonaceous allotropes in application for material science. Theoretically, graphene has a large specific surface area (2630 m² g⁻¹), high intrinsic mobility (200 000 cm² V⁻¹ S⁻¹), high Young's modulus (~10. TPa), good thermal conductivity (~5000 W m² K⁻¹), highly transparent (~97.7%), and good electrical conductivity. It is built of sp²-hybridized carbon atoms arranged in a honeycomb crystal structure. In natural graphite, the graphene layers bond together definite π - π stacking interactions.



Figure 6. Schematic representation of (a) ideal structure of AB stacked graphite, (b) structure of a graphene sheet with zig-zag and arm chair edges, and (c) HRTEM image of C-C bond at the arm chair edge in graphene.^[40]

There are several methods for preparing graphene, including mechanical stripping, liquid phase stripping, chemical vapor deposition (CVD), epitaxial growth on silicon carbide (SiC), and chemical reduction of graphene oxide. Novoselow and Geim got a success to pull apart individual graphene layer from bulk graphite using Scotch tape in 2004.^[41] This finding gave a chance to look into a properties of graphene which previously were known only in theory, but its low production rate always be a limitation. Prior to mechanical exfoliation, CVD is a non-destructive method to produce a graphene.^[42] In general, a graphene could be grow on transition metal surface (e.g., silicon wafer) with hydrocarbon gases as a carbon source at high temperature over 1000 °C. After finishing the deposit of graphene on substrate, the pure graphene layer could be obtained after chemical etching of the metal substrate. A promising method to produce a uniform and wafer-sized graphene layer is epitaxial growth on SiC. It is conducted at high temperature in the range from 1200 to 1600 °C under ultrahigh vacuum condition.^[43] Si et al. achieved light graphenes which are able to suspend well in water at a concentration (2 mg mL⁻¹) from graphene oxide by chemical reduction.^[44] They used sodium borohydride as a reducing agent and then sulfonation with aryl diazonium salt of sulfanilic acid. The chemical oxidation method is highly evaluated in a low production cost and possibility of mass production than the other methods.

Graphene oxide also has a single carbon layer and dimensions of sheets are polydisperse. Compared with graphene, this two-dimensional carbon

material has a lot of oxygen atoms on graphene oxide sheet layers that act as a functional group. In consequence, the crystal structure of graphene oxide is more complicated, and its physical and chemical properties might be changed as the transition of its structure. Many synthetic methods have been proposed as shown in Table 3.

Developer Reagent Condition Note Ref. HNO₃, KClO₃ 3-4 h, 60 °C The first method Brodie [45] Hummers HNO₃ 20 h, RT Widely used [46] David H₂SO₄, KMnO₄, NaNO₃ < 2 h, 35 °C Fast process [47] H₃PO₄, H₂SO₄, KMnO₄ 12 h, 50 °C Marcano Low toxicity [48] HNO3, H3PO4, H2SO4, KMnO4 3 h, 50 °C High yield [49] Panwar Shen $(BzO)_2$ 10 min, 110 °C No liquid [50]

Table 3. Representative Methods for Preparing Graphene Oxide.

The preparation of graphene oxide is accomplished *via* two steps and a schematic procedure described in Figure 7. In an initial step, the interlayer space of graphene layers in graphite is expanded through intercalation of an acid during the formation of graphite oxide. Consecutive oxygenations on graphite layers occur on both sides of the basal planes and result in forming graphite oxide. Exfoliation of single layers of graphite oxide leads to graphene oxide. The nature of functional groups on graphene oxide depends on the reaction condition such as shown in Table 3. Graphene oxides consist of about 45 mass% carbon in its structure but it is extremely hard to define the structure exactly due to their polydisperse characteristics.



Figure 7. Schematic synthetic procedure of graphene oxide by modified Hummer's method.^[51]

Despite the advantageous features of graphene oxide, there are common limitations such as easy agglomeration, difficult to process, and weak electrochemical activity to block expanding their application fields. To overcome this limitation, the functionalization of graphene oxide was introduced and significant progress has been achieved. The functionalization of graphene oxide not only maintains their beneficial characteristics, but also assigns additional functions to give them new characteristics. To now, the reported main stream of functionalization methods could be categorized by covalent method, non-covalent method, and element doping method. The covalent bonding functionalization enforces performance of graphene oxides by introducing organic motifs on their surface. The abundant hydroxyl groups, carboxyl groups, and epoxy groups on materials surfaces could be chemical reaction sites for isocyanation, carboxylic acylation, epoxy ring addition.^[52] opening, diazotization. and The non-covalent bond functionalization of graphene oxide leads the creation of a new composite materials. The driving forces between graphene oxides and functional groups could be π - π bond interaction,^[53] hydrogen bond interaction,^[54] ion intercalation,^[55] and electrostatic interaction.^[56] The greatest advantage of this functionalization is the final materials could maintain their intrinsic features and improve their dispersion stability which is innate limitation of graphene oxides (Figure 8).



Figure 8. Exfoliation and stabilization of graphene oxide through the π - π interaction with tetrapyrene derivative.^[53]

Element doping modifications mostly are conducted by heat treatment, ion bombardment, arc discharge, and other ways to incorporate other elements into graphene oxide layers. By introducing new elements on sheets, the surface properties such as energy band, polarity could be controlled. The common doped elements are nitrogen, boron, phosphorus, and sulfur.^[57] Although it is difficult to control quantitative doping amounts, this approach is expected to open new types of applications.

5. References

- [1] Hulin, M.; Simoni, M.; Viegi, G.; Annesi-Maesano, I. *Eur. Respir. J.* 2012, 40, 1033.
- [2] US EPA, Why Indoor Air Quality Is Important to Schools. 2015.
- [3] WHO, Household air pollution. Who.int., 2022.
- [4] ISO 16000-6:2021. ISO. https://www.iso.org/standard/73522.html (accessed 2022-12-14).
- [5] Campagnolo, D.; Saraga, D. E.; Cattaneo, A.; Spinazzè, A.; Mandin, C.; Mabilia, R.; Perreca, E.; Sakellaris, I.; Canha, N.; Mihucz, V. G.; Szigeti, T.; Ventura, G.; Madureira, J.; de Oliveira Fernandes, E.; de Kluizenaar, Y.; Cornelissen, E.; Hänninen, O.; Carrer, P.; Wolkoff, P.; Cavallo, D. M.; Bartzis, J. G. *Build. Environ.* **2017**, 115, 18.
- [6] Broderick, A.; Byrne, M.; Armstrong, S.; Sheahan, J.; Coggins, A. M. Build. Environ. 2017, 122, 126.
- [7] Du, L.; Batterman, S.; Godwin, C.; Rowe, Z.; Chin, J.-Y. Indoor Air
 2015, 25, 598.
- [8] Xu, J.; Szyszkowicz, M.; Jovic, B.; Cakmak, S.; Austin, C. C.; Zhu, J. Atmos. Environ. 2016, 141, 523.
- [9] Carazo Fernández, L.; Fernández Alvarez, R.; González-Barcala, F. J.; Rodríguez Portal, J. A. Arch. Bronconeumol. 2013, 49, 22.
- [10] Koistinen, K.; Kotzias, D.; Kephalopoulos, S.; Schlitt, C.; Carrer, P.;
 Jantunen, M.; Kirchner, S.; McLaughlin, J.; Mølhave, L.; Fernandes, E.
 O.; Seifert, B. *Allergy* 2008, 63, 810.

- [11] WHO Regional Office for Europe. WHO Guidelines for Indoor Air Quality: Selected Pollutants; WHO Regional Office for Europe: Europe, UK, 2010.
- [12] Zuraimi, M. S.; Magee, R. J.; Won, D. Y.; Nong, G.; Arsenault, C. D.; Yang, W.; So, S.; Nilsson, G.; Abebe, L.; Alliston, C. Build. *Environ.* 2018, 135, 85.
- [13] Jo, W.-K.; Yang, C.-H. Sep. Purif. Technol. 2009, 66, 438.
- [14] Xu, Z.; Yu, J.; Xiao, W. Chemistry 2013, 19, 9592.
- [15] Wenhao, J. S.; Zhang, Z. ASHRAE transactions 2005, 111, 1101.
- [16] Kadribegovic, R.; Gilligan, A.; Shi, B. ASHRAE Transactions 2011, 117.
- [17] Feng, S.; Li, D.; Low, Z.-X.; Liu, Z.; Zhong, Z.; Hu, Y.; Wang, Y.;
 Xing, W. J. Memb. Sci. 2017, 531, 86.
- [18] Zhu, Q.; Tang, X.; Feng, S.; Zhong, Z.; Yao, J.; Yao, Z. J. Memb. Sci. 2019, 581, 252.
- [19] Zadi, T.; Azizi, M.; Nasrallah, N.; Bouzaza, A.; Maachi, R.; Wolbert,
 D.; Rtimi, S.; Assadi, A. A. Chem. Eng. J. 2020, 382, 122951.
- [20] Zhang, J.; Hu, Y.; Qin, J.; Yang, Z.; Fu, M. Chem. Eng. J. 2020, 385, 123814.
- [21] Ahmad, M.; Rajapaksha, A. U.; Lim, J. E.; Zhang, M.; Bolan, N.;
 Mohan, D.; Vithanage, M.; Lee, S. S.; Ok, Y. S. *Chemosphere* 2014, 99, 19.
- [22] Kresge, C. T.; Leonowicz, M. E.; Roth, W. J.; Vartuli, J. C.; Beck, J.

S. Nature 1992, 359, 710.

- [20] Pal, N.; Lee, J.-H.; Cho, E.-B. Nanomaterials 2020, 10, 2122.
- [24] Ding, S.; Chen, J. S.; Qi, G.; Duan, X.; Wang, Z.; Giannelis, E. P.;
 Archer, L. A.; Lou, X. W. J. Am. Chem. Soc. 2011, 133, 21.
- [25] Moon, D.-S.; Lee, J.-K. Langmuir 2012, 28, 12341.
- [26] Yao, Q.; Lu, Z.-H.; Yang, K.; Chen, X.; Zhu, M. Sci. Rep. 2015, 5, 15186.
- [27] Matos, J. R.; Kruk, M.; Mercuri, L. P.; Jaroniec, M.; Zhao, L.; Kamiyama, T.; Terasaki, O.; Pinnavaia, T. J.; Liu, Y. J. Am. Chem. Soc. 2003, 125, 821.
- [28] Dekker, F.; Tuinier, R.; Philipse, A. Colloids interfaces 2018, 2, 44.
- [29] Geng, H.; Chen, W.; Xu, Z. P.; Qian, G.; An, J.; Zhang, H. Chemistry 2017, 23, 10878.
- [30] Savić, S. M.; Vojisavljević, K.; Počuča-Nešić, M.; Živojević, K.;
 Mladenović, M.; Knežević, N. Ž. Metall. Mater. Eng. 2018, 24, 225.
- [31] Manzano, M.; Vallet-Regí, M. Adv. Funct. Mater. 2020, 30, 1902634.
- [32] Zhu, L.; Shen, D.; Luo, K. H. J. Hazard. Mater. 2020, 389, 122102.
- [33] Al-Absi, A. A.; Mohamedali, M.; Domin, A.; Benneker, A. M.; Mahinpey, N. Chem. Eng. J. 2022, 447, 137465.
- [33] Poorakbar, E.; Shafiee, A.; Saboury, A. A.; Rad, B. L.; Khoshnevisan,
 K.; Ma'mani, L.; Derakhshankhah, H.; Ganjali, M. R.; Hosseini, M. *Process Biochem.* 2018, 71, 92.
- [35] Zhou, Y.; Quan, G.; Wu, Q.; Zhang, X.; Niu, B.; Wu, B.; Huang, Y.;

Pan, X.; Wu, C. Acta Pharm. Sin. B. 2018, 8, 165.

- [36] Xu, Y.; Kutsanedzie, F. Y. H.; Hassan, M.; Zhu, J.; Ahmad, W.; Li,
 H.; Chen, Q. Food Chem. 2020, 315, 126300.
- [37] Bagheri, E.; Alibolandi, M.; Abnous, K.; Taghdisi, S. M.; Ramezani, M. J. Mater. Chem. B Mater. Biol. Med. 2021, 9, 1351.
- [38] Ali, N. S.; Alismaeel, Z. T.; Majdi, H. S.; Salih, H. G.; Abdulrahman, M. A.; Cata Saady, N. M.; Albayati, T. M. *Heliyon* 2022, 8, e09737.
- [39] Lipson, H.; Stokes, A. R. Nature 1942, 149, 328.
- [40] He, K.; Lee, G.-D.; Robertson, A. W.; Yoon, E.; Warner, J. H. Nat. Commun. 2014, 5, 3040.
- [41] Novoselov, K. S.; Geim, A. K.; Morozov, S. V.; Jiang, D.; Zhang, Y.;
 Dubonos, S. V.; Grigorieva, I. V.; Firsov, A. A. Science 2004, 306, 666.
- [42] Van Bommel, A. J.; Crombeen, J. E.; Van Tooren, A. Surf. Sci. 1975, 48, 463.
- [43] Huang, H.; Chen, S.; Wee, A. T. S.; Chen, W. Graphene 2014, 177.
- [44] Si, Y.; Samulski, E. T. Nano Lett. 2008, 8, 1679.
- [45] Brodie, B. C. XIII. Philos. Trans. R. Soc. Lond. 1859, 149, 249.
- [46] Hummers, W. S., Jr; Offeman, R. E. J. Am. Chem. Soc. 1958, 80, 1339.
- [47] López-Díaz, D.; Velázquez, M. M.; Blanco de La Torre, S.;
 Pérez-Pisonero, A.; Trujillano, R.; García Fierro, J. L.; Claramunt, S.;
 Cirera, A. Chemphyschem 2013, 14, 4002.

- [48] Marcano, D. C.; Kosynkin, D. V.; Berlin, J. M.; Sinitskii, A.; Sun, Z.; Slesarev, A.; Alemany, L. B.; Lu, W.; Tour, J. M. ACS Nano 2010, 4, 4806.
- [49] Panwar, V.; Kumar, A.; Singh, R.; Gupta, P.; Ray, S. S.; Jain, S. L. Ind. Eng. Chem. Res. 2015, 54, 11493.
- [50] Shen, J.; Hu, Y.; Shi, M.; Lu, X.; Qin, C.; Li, C.; Ye, M. Chem. Mater. 2009, 21, 3514.
- [51] Kovtyukhova, N. I.; Ollivier, P. J.; Martin, B. R.; Mallouk, T. E.; Chizhik, S. A.; Buzaneva, E. V.; Gorchinskiy, A. D. Chem. Mater. 1999, 11, 771.
- [52] Chua, C. K.; Pumera, M. Chem. Soc. Rev. 2013, 42, 3222.
- [53] Song, P.; Xu, Z.; Wu, Y.; Cheng, Q.; Guo, Q.; Wang, H. Carbon 2017, 111, 807.
- [54] He, M.; Zhang, R.; Zhang, K.; Liu, Y.; Su, Y.; Jiang, Z. J. Mater. Chem. A Mater. Energy Sustain. 2019, 7, 11468.
- [55] Choi, E.-Y.; Han, T. H.; Hong, J.; Kim, J. E.; Lee, S. H.; Kim, H. W.; Kim, S. O. J. Mater. Chem. 2010, 20, 1907.
- [56] Bhunia, P.; Hwang, E.; Min, M.; Lee, J.; Seo, S.; Some, S.; Lee, H. Chem. Commun. 2012, 48, 913.
- [57] Duan, X.; Indrawirawan, S.; Sun, H.; Wang, S. Catal. Today 2015, 249, 184.

Chapter 2.

Surface-Modified Wrinkled Mesoporous Silica as an Effective Adsorbent for Benzene, Toluene, Ethylbenzene, and Xylene in Indoor Air

* This chapter is slightly modified version of the article: <u>Shim, I.-K.</u>; Kim, J.; Lee, J. K.; Oh, J.-M.; Park, J. K. *ACS Appl. Nano Mater.* 2022, 5(12), 18138-18148. http://doi.org/10.1021/acsanm.2c04032

1. Introduction

During the COVID-19 pandemic, indoor air quality has become an emerging health concern. Furthermore, micron-sized particulate matter (PM 2.5) is a known air pollutant. The effects of greenhouse gas, which is an air pollutant that causes global climate changes, have emerged as a critical environmental issue. In addition, PM 2.5 can induce climate changes, and the inhalation of PM 2.5 can cause various health problems in humans. Therefore, volatile organic compounds (VOCs), which are precursors of PM 2.5 that are toxic to humans, have been classified as the most serious air pollutants; furthermore, the development of technologies to capture these pollutants is in high demand.^[1-5]

Porous materials such as activated carbon, zeolites, mesoporous silicates, pillared clays, and metal-organic frameworks, are promising candidates as adsorbents for the removal of air pollutants.^[6-10] The rapid adsorption and large adsorption capacity of porous materials are ascribed to their large surface areas and unique pore structures. However, it has been previously reported that the pore size, surface nature, chemical stability, and internal porous structure also determine the adsorption performance of porous materials.^[11-14] For example, porous materials with hydrophilic surfaces are not suitable adsorbents for VOCs in the air because of the hydrophobic properties of VOCs. To overcome this limitation and promote the selectivity of adsorbents for VOCs, the chemical properties of adsorbent surfaces can be easily modified to match the chemical properties of adsorbates using

cost-effective and simple chemical manipulation methods.^[15,16] Therefore, two methods have been used to modify the surfaces of porous materials: 1) one-pot synthesis using specific surface-modification reagents during the preparation of porous materials and 2) post-synthesis using surface modification reagents.^[17,18] The latter is a more powerful method than the former as the fabricated materials, and in particular silica-based materials, present high mechanical strength and easily tunable pore structures.

VOCs are ubiquitous pollutants that are primarily responsible for the sick building syndrome and multiple chemical sensitivities.^[19,20] Among VOCs, benzene, toluene, ethyl benzene, and xylenes (BTEX) are the most representative and harmful chemicals in indoor air.^[21] BTEX are detected almost exclusively indoors (frequency > 95%), and benzene has been classified as a Group 1 carcinogenic to humans by the International Agency for Research on Cancer.^[22,23] BTEX are released continuously from the surfaces of building materials, wood products, electronics, and clothes over extended periods; therefore, they accumulate in indoor air.^[24]

Several researchers have attempted to lower the concentration of BTEX in indoor air by using various porous adsorbents, including surface-modified porous adsorbents.^[25] However, previous studies presented common limitations, as follows: 1) one or several adsorbates were tested individually, although numerous VOCs are present in real indoor air; 2) it is challenging to adjust the hydrophobicity of silica-based adsorbents; and 3) it is challenging to fine-tune the porosity of adsorbents to optimize their

adsorption properties owing to the robust nature of ceramic bonds. To overcome these shortcomings, we prepared several spherical wrinkled silicates with different surface chemical properties using a sol-gel method, exposed them to a mixed BTEX atmosphere to simulate real indoor air, and evaluated the selectivity of the adsorbents for the adsorbates (Scheme 1).



Heating Coil for Thermal desorption TD

Scheme 1. Schematic of the (a) Fabrication of Wrinkle-Structured Silica Nanoparticles and (b) Standard BTEX Adsorption Test Method Based on the International Standard ISO 16017-1:2000 Using the Materials Fabricated in This Study.

As it is necessary to develop a facile way to transfer the fundamental research efforts to the lots of commercial applications, we believe all challenging issues aforementioned should be demonstrated in cost-effective ways. In this purpose, the wrinkled silica nanoparticle (WSN) was introduced as the host materials because i) this material could be prepared in relatively mild condition compared with other silicates and ii) the porosity and particle size are easily controlled in a solution process. Furthermore, the surface of WSN could be subjected to further modification with various silane compounds to impose the desirable properties for the effective adsorbates toward BTEX gases mixed in indoor air.

2. Experimental

2.1. Chemicals and instrumentation

Cetyltrimethylammonium bromide (CTAB), tetraethyl orthosilicate (TEOS), BTEX analytical standard (200 μ g/mL), n-octyltriethoxysilane (OTES), hexadecyltrimethoxysilane (HDTMS), and triethoxyphenylsilane (TEPS) were obtained from Aldrich. Urea, cyclohexane, n-butanol, ethanol, and acetone were purchased from Samchun Chemicals. The chemicals were used as received without further purification.

The size and morphology of the samples were observed using an H-4300 (Hitachi) field-emission scanning electron microscopy (FE-SEM) instrument

and an H-7600 (Hitachi) high-resolution transmission electron microscopy (HR-TEM) device.

Thermogravimetric analysis (TGA) data were collected using a STA6000 (PerkinElmer) system in the temperature range of 30-800 °C at a heating rate of 10 °C min⁻¹ under an air atmosphere. N₂ adsorption-desorption experiments were performed using a Belsorp II (BEL Japan) apparatus at liquid N₂ temperature (77 K), and the specific surface areas of the adsorbents were estimated using the Brunauer-Emmett-Teller (BET) method.

Fourier-transform infrared (FT-IR) spectra were acquired using a Frontier (PerkinElmer) FT-IR spectrometer and the KBr pellet method in the wavenumber range of 400-4000 cm⁻¹, and the results were used to confirm the formation of organosilane grafts on the surface of the wrinkled silica nanoparticles (WSNs) used as adsorbents.

The BTEX adsorbed on the WSNs were desorbed using a thermal desorption system, their concentrations were determined, and then they were separated using an GC-2010 (Shimadzu) gas chromatograph, followed by detection using a quadrupole mass spectrometer. A VB-1 capillary column (VICI; 0.25 mm internal diameter, 60 m length, 1.0 μ m film thickness) was used as the analytical column. The temperature program of the gas chromatography oven was as follows: -40 °C for 6 min, increased at a rate of 4 °C min⁻¹ to 180 °C, increased at a rate of 20 °C min⁻¹ to 250 °C, and then maintained at 250 °C for 10 min.

2.2. Preparation of mesoporous WSNs

Mesoporous WSNs were prepared using our previously reported method with some modifications.^[26] In brief, 13 mmol of CTAB and 50 mmol of urea were dissolved in 150 mL of ultrapure water, and then 60 mmol of n-butanol (*n*-BuOH) was added to the mixture under stirring until the mixture became transparent. Next, 1.4 mol of cyclohexane and 60 mmol of TEOS were added simultaneously to the reaction mixture, and the solution was stirred for 30 min. The mixture was then heated to 70 °C and maintained at this temperature for 16 h. The obtained precipitate was isolated via centrifugation and washed several times with acetone and ethanol. Lastly, the surfactant was extracted from the WSNs by redissolving the precipitate in a 10% volume of a 12 M HCl solution in ethanol under vigorous stirring at room temperature for 15 h.

2.3. Surface modification of WSNs

Three silane coupling reagents: OTES, HDTMS, and TEPS, were used to modify the surface of the surfactant-extracted WSNs (SE-WSNs) using conventional hydrolysis condensation reactions. Typically, 200 mg of SE-WSNs was dispersed in 100 mL of absolute ethanol, and 0.5 mol of silane, which was used as the coupling agent, was added to the dispersion. The mixture was refluxed for 12 h under vigorous stirring and then centrifuged. The precipitates were washed a few times with ethyl alcohol and dried overnight at 80 °C.

2.4. BTEX adsorption performance of WSNs

The experimental procedure was based on the international standard ISO $16017-1:2000.^{[27]}$ Four sorbent samples were prepared by individually packing 50 mg of SE-WSNs, OTES-WSNs, HDTMS-WSNs, and TEPS-WSNs with quartz wool in thermal desorption glass tubes (1/4" OD × 3.5" length; Supelco), which were subsequently sealed.

To quantify the amount of adsorbent, each tube was connected in series with a back tube containing pre-cleaned commercial sorbent Tenax TA (a porous polymer resin based on 2,6-diphenyl-p-phenylene oxide). BTEX standard solution (1 μ L) was injected into the linked test tubes at 200 °C using an 80 mL min⁻¹ N₂ gas stream.

The concentrations of adsorbed BTEX were calculated by subtracting the amounts of BTEX in the back tube from the amounts of BTEX in the spiked sample. The percentages of adsorbed BTEX in each test tube were calculated as follows:

% BTEX adsorbed = $(C_s - C_b) \times 100$,

where C_s is the concentration of BTEX in the spiked standard sample and C_b is the concentration of BTEX in the back tube.

3. Results and Discussion

3.1. Sample characterization

WSNs were fabricated using a simple reverse micelle method and cyclohexane as the oil phase. It was hypothesized that *n*-BuOH, which is an amphiphilic solvent, conferred the wrinkled pore structure to WSNs because of the dynamic equilibrium between the oil and water phases. Therefore, the reverse micelles formed by CTAB were slightly deformed, and n-BuOH penetrated them, promoting the migration of a small amount of oil phase into the water phase. The kinetically formed nanostructures were then solidified as TEOS was hydrolyzed inside the nanostructures at 70 °C for 16 h. After CTAB was removed via a subsequent extraction step, the as-prepared WSNs particles were subjected to surface modification with OTES, HDTMS, and TEPS to adjust their hydrophobicity. Besides, such silane derivatives for the surface modification were selected by concerning both molecular structures and chain length of functional groups in the silane moiety. In general, adsorption between host and guest compounds is influenced by molecular shapes and molecular interactions. Therefore, it was worthy to demonstrate what factors such as molecular shape and chain length (octyl groups in OTES and hexadecyl groups in HDTMS) would be important to design host materials in terms of target-specificity. Because all BETX gas molecules have planar benzene motifs, it could be expected that phenyl groups in TEPS which can provide π - π interaction would well fit to BTEX. Furthermore, OTES and HDTMS modification is anticipated to

induce van der Waals interaction between host and BTEX. By comparing the adsorption efficacy on modified hosts, we could determine the molecular interaction strength between π - π interaction and van der Waals interaction that is usually influenced by chain length and/or contact area.



Figure 1. Scanning electron micrographs (top panels) and transmission electron micrographs (bottom panels) of WSNs.

Figure 1 shows the FE-SEM and HR-TEM images of the as-prepared WSNs. The synthesized WSNs presented a uniform and spherical morphology, with diameters in the range of 200-400 nm. The HR-TEM

images revealed that the WSNs presented an irregular mesoporous surface texture with an average pore width of approximately 30 nm comprising wrinkled silica. Furthermore, the inner pore structures were continuously wrinkled silica from the top surfaces, which was confirmed using HR-TEM. However, the silica struts and/or networks were not porous and comprised densely packed wrinkled silica structures in the center. Therefore, the porosity of WSNs was primarily ascribed to their somewhat large mesopores. In addition, detailed morphology analysis indicated that the WSNs could be formed in the wrinkled or deformed reverse micelles owing to *n*-BuOH penetrating the micelles (Scheme 1a). The detailed reaction mechanism for the formation of hierarchical mesoporous WSNs has been described in our previous paper.^[26]

The FT-IR spectra of the SE-WSNs and surface-modified WSNs were analyzed to confirm their chemical compositions (Figure 2). The silica frameworks of WSNs were confirmed by the presence of the distinctive bands at 3436, 1090, 960, 803, and 468 cm⁻¹, which were assigned to the O-H stretching vibration, Si-O-Si asymmetric stretching, Si-O-Si-OH vibration, Si-O-Si symmetric stretching, and Si-O-Si bonding modes, respectively.^[28] Unlike the FT-IR spectrum of SE-WSNs, those of the surface-modified WSNs included the characteristic vibration bands of organosilane functionalities (the blue and dotted lines in Figure 2). These results confirmed that the SE-WSNs did not contain significant amounts of surfactants.



Figure 2. FT-IR spectra of (a) SE-WSNs, (b) OTES-WSNs, (c) HDTMS-WSNs, and (d) TEPS-WSNs.

Even though the lengths of the aliphatic chains of OTES-WSNs and HDTMS-WSNs were different, their FT-IR spectra were comparable because of the similarities between their functional groups. The peaks at 2850, 2917, and 2956 cm⁻¹ in the FT-IR profiles of OTES-WSNs and HDTMS-WSNs were assigned to the symmetric and asymmetric stretching modes of the methylene groups and asymmetric stretching mode of the methyl group, respectively.^[29] The characteristic peaks for C-H stretching in the FT-IR

spectrum of TEPS-WSNs were attributed to the vibrational mode of C_{sp2} -H and were upshifted to wavenumbers in the range of 2980–2850 cm⁻¹ compared to those in the FT-IR spectra of OTES-WSNs and HDTMS-WSNs.^[30,31]

In general, the surface modification methods of porous nanoparticles via post-grafting techniques including the method in this study always have the issue of how to technically control the reactivity of exterior and interior surfaces because both sides of surfaces may have similar reactivity in terms of chemistry. However, there clearly exist topological differences between the exterior and interior surface, and thus the molecular accessibility of both surfaces would be different. This topology issue is strongly related to the fact that the chemical reactions are generally depending on the diffusion rates of materials in the reaction media. While the exterior surface is fully exposed for chemical reaction, the interior surface was only open for the molecules which penetrated the narrow pathways to reach the interior part. Therefore, it could be expected that the chemical reactions in exterior and interior surfaces could be controlled in such different accessibility of materials with different diffusion rates in the reaction media. We empirically found the optimum concentration at which the reaction mainly occurs at exterior modification forming very thin layers. The rationales on the exterior surface modification were obtained based on substantial studies together with the characteristics of host WSNs.



Figure 3. Thermogravimetric analysis curves of as-prepared WSNs, SE-WSNs, OTES-WSNs, HDTMS-WSNs, and TEPS-WSNs.

The TGA curves of the WSNs (Figure 3) further confirmed that OTES, HDTMS, and TEPS were grafted on SE-WSNs. The weight loss of SE-WSNs in the temperature range of 200–400 °C was significantly lower than that of the as-prepared WSNs because of the effective removal of surfactant from the pores of SE-WSNs. Hence, the primary weight loss stage of the as-prepared WSNs was ascribed to the bonding water and dihydroxylation on their surface. The surface-modified WSNs also exhibited a rapid weight loss stage starting at approximately 240 °C, which was

smaller than that of the as-prepared WSNs. Therefore, it was suggested that the weight losses of the surface-modified WSNs corresponded to the oxidative decomposition of the organic components of the organosilanes grafted onto the surface of WSNs. The weight loss ratios of the as-prepared WSNs, SE-WSNs, OTES-WSNs, HDTMS-WSNs, and TEPS-WSNs were 23.9%, 8.4%, 10.2%, 11.0%, and 11.1%, respectively. Therefore, it was concluded that the organosilanes covered the surface of SE-WSNs during the surface-modification reactions. Besides, based on the significantly smaller weight loss ratios from modified samples than that from as-prepared WSNs, it could be expected that modified WSNs still had quite large amounts of void volumes.

The specific surface areas and pore structures of the adsorbents were obtained using their N_2 adsorption-desorption isotherms (Figure 4), and the results are summarized in Table 1. The adsorbents presented similar type IV isotherms, indicating their mesoporous nature, according to the classification of Brunauer, Deming, Deming, and Teller.^[32] Furthermore, the isotherms presented sharp capillary condensation at a relative pressure of approximately 0.9 owing to the relatively large mesopores (30 nm) of the samples, as confirmed by the SEM and TEM data.



Figure 4. N₂ adsorption-desorption isotherms of the as-prepared WSNs, SE-WSNs, OTES-WSNs, HDTMS-WSNs, and TEPS-WSNs.

Although the isotherms of the surface-modified WSNs were quite similar to those of the unmodified WSNs, the isotherms of the surface-modified WSNs presented H3 hysteresis loops. This suggested that the surface-modified WSNs presented slit-shaped and/or panel-shaped pores.^[33] These results were consistent with the SEM and TEM data (Figure 1).

Unlike the isotherms, the specific surface areas and mean pore sizes of the surface-modified WSNs were affected by the anchored organosilanes. After surfactant extraction, the specific surface area of SE-WSNs increased significantly from 387 to 650 m² g⁻¹. As the silanol groups on the SE-WSNs surface were replaced with organosilanes via condensation reactions, the specific surface areas of the surface-modified WSNs decreased gradually and ranged between 517 and 630 m² g⁻¹.

The calculated Barrett-Joyner-Halenda (BJH) pore distribution peaks of the as-prepared WSNs, SE-WSNs, OTES-WSNs, HDTMS-WSNs, and TEPS-WSNs were 24.4, 37.4, 37.4, 32.3, and 32.3 nm, respectively. The decrease in mesopore size after surface modification was attributed to organosilane coating the surface of the SE-WSNs. The pore widths of the adsorbents are summarized in Table 1.

	BET			BJH		
Sample	$\frac{S_{\rm BET}^{a}}{(m^2 g^{-1})}$	$V_{\rm p}^{\rm b}$ (cm ³ g ⁻¹)	D ^c (nm)	$\frac{A_{\rm p}^{\rm d}}{({\rm m}^2{\rm g}^{-1})}$	$d_{p,peak}^{e}$ (nm)	$V_{\rm p}^{\rm b}$ (cm ³ g ⁻¹)
As-prepared WSNs	387	1.80	18.66	441	24.41	1.82
SE-WSNs	650	1.63	10.00	635	37.44	1.60
OTES-WSNs	517	1.61	12.47	469	37.44	1.57
HDTMS-WSNs	599	1.91	12.73	558	32.28	1.87
TEPS-WSNs	630	1.59	10.06	594	32.28	2.08

Table 1. Structural Properties of the Wrinkled Silica Nanoparticles.

^a Specific surface area; ^b Mean pore volume; ^c Mean pore diameter; ^d Pore specific surface area; ^e Pore distribution peak.

However, unlike the average pore sizes (D) listed in Table 1, which depended on the organosilane used for surface modification, the BJH pore width distributions of the surface-modified WSNs and SE-WSNs significantly showed detail pore structures depending on the organic moieties of the organosilanes (Figure 5a).

a)



Figure 5. (a) BJH pore size distribution of WSNs, SE-WSNs, OTES-WSNs, HDTMS-WSNs, and TEPS-WSNs. (b) Schematic of the rationale for the difference in pore size distributions between WSNs modified with different organosilanes.

First of all, the pore distributions of modified WSNs such as OTES-WSNs, HDTMS-WSNs and TEPS-WSNs were similar, but the pore volume peak of OTES-WSNs at similar pore widths was little lower than those of other two types of modified WSNs. However, the pore volume distribution of SE-WSNs was broad and did not exhibit discernable peak pore volume positions at specific pore widths. Presumably, this unique feature would happen as the walls of WSN particles were irregularly and slightly shrunk when they were dried without the support of surfactant molecules in interior surfaces of particles. Furthermore, the distribution profiles of modified WSNs were more similar with that of as-prepared WSNs rather than that of SE-WSNs would. Therefore, it was hypothesized that these distribution trends indicated different pore width development progress upon the treatment of post-modification process. (Figure 5b).

In this study, we lacked detailed information on the thickness of the organosilane layers of the surface-modified WSNs. We hypothesized that organosilanes formed thin coating layers on the surface of WSNs because the BET surface areas of the surface-modified WSNs were slightly lower than that of SE-WSNs without significantly blocking the pore widths. However, the pore volumes of modified WSNs ranging from 2 nm to 10 nm were smaller than that of SE-WSNs. Especially, the BET surface areas could be listed in the largest to smallest order as SE-WSNs > TEPS-WSNs > HDTMS-WSNs > OTES-WSNs > As-prepared WSNs, which was same

order as amount of pore volumes at ranging from 2 nm to 10 nm listed in the largest to smallest order (Figure 5a). Therefore, it could be implied that the surface area of all WSN particles mainly relied on the portion of pores ranging from 2 nm to 10 nm. Then, the average size of particles would be maintained as estimated in TGA showing small fractions of weight loss implying the increase in thickness of modified WSNs were negligible. In addition, small molecules such as TEPS molecules could be more accessible toward interior surfaces than the other long-chained silane molecules but the pore volumes of TEPS-WSNs ranging from 2 nm to 10 nm were larger than those of other modified WSNs. Therefore, it could be expected that the surface modification reagents would not be easily diffused into the interior surfaces once the exterior surfaces were modified in a kinetically faster fashion. Moreover, it could be worthy to suggest that the modified layers would be very thin on modified WSN particles and large fractions of interior surfaces with over 10 nm pore widths would still remain intact. Typically, the π - π interactions in the benzene ring in the gas phase are stronger than the van der Waals forces. Nonetheless, the benzene rings of TEPS are far from each other owing to their degree of rotation and steric hindrances (Figure 5b). Therefore, this type of kinetic motion of phenyl rings around the pores of WSNs would not significantly block the pore windows inducing a quite symmetrical shape of peak around the peaked position in its pore size distribution profile as shown in Figure 5a.

In contrast, the alkyl chains of OTES and HDTMS were more closely

packed than the phenyl rings of TEPS, and steric hindrances were weaker. Although the degree of rotational freedom of alkyl chains can be similar to that of the rotation of phenyl rings, long alkyl chains can form various conformational isomers, such that the conformers entangle the chains, resulting in dense close packing (Figure 5b). Even though the intermolecular van der Waals interactions between two molecules in the gas phase are weaker than the π - π interaction forces, van der Waals forces could render strong forces upon being closer and denser. Hence, although the kinetic motion of alkyl chains around the pore windows of porous nanoparticles frequently could induce the formation of slit-like and irregular pore windows somewhat blocking the pores than the kinetic motion of phenyl rings, the longer alkyl chains having more than 4 carbons would be more severely entangled and supported with each other (Figure 5b). As a result, the longer alkyl chains could form less slit-like and irregular pore windows and less blocking pore width. Therefore, the peaked pore volume of HDTMS-WSNs could be closer to that of TEPS-WSNs than that of OTES-WSNs in their pore size distribution profiles and the more symmetrical shape around the peak position as shown in Figure 5a.

3.2. VOC Adsorption capacities of WSNs

Figure 6a shows the VOC adsorption capacities of SE-WSNs, OTES-WSNs, HDTMS-WSNs, and TEPS-WSNs at room temperature. Air samples spiked with 200 ng of ethylbenzene and xylene, which are more

hydrophobic than benzene and toluene were purified using 50 mg of each adsorbent. However, the adsorption efficiencies of the adsorbents for benzene and toluene depended on the surface properties of the adsorbents. In particular, the adsorption efficiencies of the adsorbents for benzene were significantly different, and SE-WSNs, OTES-WSNs, HDTMS-WSNs, and TEPS-WSNs eliminated 82.6%, 77.3%, 99.0%, and 52.7% of benzene, respectively, from spiked air samples. The adsorption of gas molecules by porous materials can be affected by the gas-pore-surface interaction energy, pore diameter, pore volume, pore specific surface area, pore morphology, and surface roughness.^[34] In terms of specific surface area, it was expected that the adsorption capacity of TEPS-WSNs (surface area of 630 m² g⁻¹) for benzene be higher than those of OTES-WSNs and HDTMS-WSNs (surface areas of 517 and 599 m^2 g⁻¹, respectively). However, the experimental results differed from the expectation, suggesting that factors other than the specific surface area of the adsorbent contributed to the adsorption performance to a greater extent. The benzene adsorption capacities of OTES-WSNs and HDTMS-WSNs differed by more than 20% even though their surfaces were covered with similar organic silanes with different alkyl chain lengths. Typically, the absorption performance of the materials in this study for BTEX was attributed to the capillary condensation of sorbates in the large mesopores of the adsorbents, and the adsorption capacities of SE-WSNs for BTEX were proportional to the molecular weights of the adsorbates and molecular interactions between adsorbates and adsorbents. The

boiling points of benzene, toluene, ethyl benzene, and para-xylene are 80.1, 110.6, 136, and 144 °C, respectively.

However, to further investigate the differences in adsorption capacity between adsorbents, the values of the interaction energies for several benzene-hydrocarbon clusters were retrieved from the literature,^[35-37] and are summarized in Table 2.

Table 2. Estimated Interaction Energy (ΔE_{int})Values for SeveralBenzene-Hydrocarbon Clusters.

		Deference			
		Sandwich	T-shaped	T-shaped(2)	Kelelelice
benzene-methane	-1.16 ^a				40
benzene-ethane	-1.98^{b}				38
benzene-propane	-2.54^{b}				38
benzene-n-butane	-3.05 ^b				38
benzene-benzene		-1.80 ^c	-2.62 ^c	-2.62 ^c	39
benzene-toluene		-2.27 ^c	-2.55 ^c	-2.95 ^c	39

^{*a*} Calculated CCSD(T) level interaction energy using the aug-cc-pVDZ; ^{*b*} Estimated CCSD(T) interaction energy at the basis set limit; ^{*c*} Estimated CCSD(T) interaction energy using the aug-cc-pVTZ

Fujii *et al.*^[38] and Shibasaki *et al.*^[39] determined the CH- π interaction energy values in benzene-alkane model clusters using laser spectroscopy experiments and theoretical calculations. In addition, Sinnokrot and Sherrill^[40] calculated the lowest conformational energy between two benzene molecules using a high-level quantum mechanical method. Fujii *et al.*^[38] reported that the interaction energy increased proportionally with the alkyl chain length. However, the energy depended on the arrangement of the two benzene molecules (face-to-face, edge-to-face, and parallel-displaced stacking) and ranged between 1.80 and 2.62 kcal mol^{-1} . Typically, aromatic-aromatic interactions are stronger than aromatic-aliphatic interactions owing to the π - π stacking interactions between aromatic rings. However, the aromatic-aliphatic interaction energy for aliphatic hydrocarbons with long chains (n > 4; 2.7 kcal mol^{-1}) can exceed the benzene-benzene interaction energy (1.8-2.62) kcal mol⁻¹). These findings indicate that the hydrophobic effect, difference in interaction energy between adsorbent and adsorbate, and adsorbate surface area affected the total adsorption efficiencies of individual VOCs on the surface-modified WSNs. Dispersion forces are the critical factor affecting the interaction forces for benzene-alkane clusters. Dispersion forces, which are the weakest intermolecular attraction forces, are attributed to the surrounding dipole moments. The greater the polarizability, the stronger the dispersion forces, which strengthen the attraction between molecules with larger molecular masses. The following equation can be used to quantify the strength of the interactions between dissimilar atoms or molecules (A and B) from the viewpoint of polarizability and dispersion forces:^[41]

$$V = \frac{-3}{2} \frac{I_A I_B}{I_A + I_B} \frac{\alpha_A \alpha_B}{r^6}$$

where r is the distance and I is the first ionization energy between atoms or molecules and α is the polarizability constant.


Figure 6. (a) Adsorption capacities of SE-WSNs, OTES-WSNs, HDTMS-WSNs, and TEPS-WSNs for BTEX and (b) schematic illustration for their adsorption properties.

Therefore, the dispersion energy and polarizability of long alkane moieties (i.e. HDTMS) were considerably higher than those of short alkane moieties

(i.e. OTES). Consequently, the adsorption capacity of HDTMS-WSNs for benzene was higher than that of OTES-WSNs. Moreover, toluene, which is more hydrophobic than benzene, can be easier adsorbed onto hydrophobic surfaces, such as those of OTES-WSNs, HDTMS-WSNs, and TEPS-WSNs, and the adsorption capacities illustrated in Figure 6b reflecting these facts. However, the rationale for the lowest absorption capacity of TEPS-WSNs for benzene has not yet been elucidated, even though interaction energy was considered. Therefore, we suggested that the intermolecular interactions between benzene and the phenyl groups of TEPS-WSNs prevented the capillary condensation of benzene molecules in the mesopores of TEPS-WSNs (Figure 6b).

As we quantitatively discussed on the molecular interaction between carbon groups from the literatures of Fujii *et al.* and Shibasaki *et al.* (please see Table 2), the interaction between aromatic groups and alkyl groups normally is weaker than that between aromatic and aromatic groups but the interaction between aromatic groups and alkyl groups having more than 4 carbons can be greater than that of aromatic-aromatic interaction. In this study, the numbers of carbon functionalities in OTES and HDTMS were 8 and 16, respectively. Therefore, it could be anticipated that the BTEX would be more accumulated and gathered around the exterior surfaces of WSNs modified with OTES and HDTMS than the surfaces of TEPS-WSNs to be facilely fill the mesopores of modified WSNs. Although, if the layer formed via modification with TEPS was thick enough to densely expose phenyl

groups to exterior surfaces of WSNs, the BTEX molecules could be captured by many phenyl groups in the layers of TEPS groups. Moreover, the low adsorption performance of TEPS-WSNs for benzene and toluene were well matched with the trends obtained from theoretical calculations (Table 2) between two single molecules. Therefore, it could be expected that the thickness of modified layers grown on the surface of WSNs would be thin in the level of almost monolayer.

Table 3. The Summary of Recent Works and WSNs Adsorbents Used inThis Study.

Materials	Adsorptio	on efficacy	Surface			
	Benzene	Toluene	Ethyl- benzene	o-Xylene	$(m^2 g^{-1})$	Reference
SE-WSNs	0.042	0.043	0.038	0.025	387	
OTES-WSNs	0.040	0.041	0.038	0.025	650	This
HDTMS-WSNs	0.051	0.043	0.038	0.025	517	work
TEPS-WSNs	0.027	0.040	0.038	0.025	630	
TMS-RH ^a	0.007	0.020	0.149	0.061	632	Areerbo
Carbograph 4 ^b	0.018	0.079	0.180	0.036	210	et al. ^[42]

^{*a*} Trimethylchlorosilane grafted MCM-41(mesoporous silica)

^b Commercial adsorbent(graphitized carbon black)

The summary of toxic gas adsorption performances for various WSNs was shown in Table 3 together with those of other materials obtained from similar systems. Therefore, it was found that all the WSNs in this study showed significantly higher adsorbed amounts for benzene than others in terms of the adsorbed amounts in the unit amount of adsorbates. Interestingly, while the others showed high adsorbed amount for specifically favorable guests, WSNs demonstrated mild preference for most BTEX gases. Therefore, it could be suggested that the WSNs could be versatile adsorbates for the benzene-derivative VOCs.

The MCM-41 modified with trimethyl silane (TMS) and commercially available Carbograph showed the best adsorption performance with the ethyl benzene among BTEX (Table 3) because the hydrophobic compatibility between host and guest was the most matched with ethylbenzene. Thus, the van der Waals interaction between hosts and guests could govern the preferential adsorption. However, WSNs generally showed similar adsorption performances for BTEX molecules (Table 3) without the special preference. As illustrated in Figure 5(b), the outer surface of WSN was modified with organic moiety and according to the N₂ adsorption/desorption isotherms (Figure 4), the pronounced capillary condensation of adsorbates was observed in the high relative pressure regimes. This could be due to the condensation adsorbates mesoporous of in the worm-like capillaries of WSNs. Accordingly, the organic modification on the surface of WSN could be utilized to concentrate BTEX molecules around the mesopore windows, and the adsorbates were condensed in the capillaries. Therefore, it could be expected that the adsorption performances of WSNs were synergistically determined by considering both hydrophobicity like other materials (Table 2)

and capillary condensation tendency upon expanding alkyl chain length (Figure 6).

Then, to confirm the recyclability of WSNs, the columns of all materials were purged with blowing N_2 gas at the flow rate of 100 mL min⁻¹. and heating at 200 °C for 10 minutes to regenerate the surfaces of adsorbates. The typical regeneration temperatures on Tenax TA (international standard for BTEX) are summarized in Table 4.

Table 4. The Summary of Boiling Points for BTEX and DesorptionTemperature from Tenax TA That Is the Commercially Available andInternational Standard Materials as Demonstrated in ISO 16017-1:2000.

	Benzene	Toluene	Ethylbenzene	Xylene
Boiling point (°C)	80	111	132-144	136
Desorption temperature from Tenax TA ^{<i>a</i>} (°C)	120	140	140	145

^a Tenax TA: a porous polymer resin based on 2,6-diphenyl-p-phenylene oxide.

Different from the temperature for Tenax TA tubes, the columns of WSNs were heated up to 200 °C which was determined by concerning thermal characteristics of adsorbents and adsorbates such as the thermal decomposition of organic layers on WSNs and boiling points. Then such performances were consecutively cycled for five times. The result exhibited that the adsorption efficacy for benzene and toluene was not significantly altered upon consecutively recycling up to five times as shown in Figure 7.

Moreover, it was also confirmed that the WSNs were thermally stable up to 200 °C in repeating cycles.



Figure 7. The recyclability profiles of various WSNs.

The most WSNs except TEPS-WSN showed quite constant performances for both benzene and toluene at each recycle with considering the standard deviations. Nonetheless, TEPS-WSN showed quite considerable discrepancy in the adsorption performances for benzene between on the initial (0 point in Figure 7) and the first recycle but it did not show significant discrepancy in the consecutive adsorption performance for toluene. Therefore, it could be expected that some amount of benzene could be easily stuck in the TEPS motifs due to the well-matched hydrophobic and shape compatibility between phenyl group in TEPS and benzene.

4. Conclusions

Spherical WSNs (300 nm) were synthesized. Their surface was chemically modified with three organosilanes to convert them into adsorbents for the removal of frequently detected VOCs from indoor air. The factors affecting the adsorption efficiency of the surface-modified WSNs for BTEX were investigated. In addition to the surface area, pore size, and pore volume of the adsorbents and adsorbate-adsorbent interaction energies, the dispersion forces between adsorbents and adsorbates were among the critical factors affecting VOC adsorption. Although the organosilanes grafted onto the surface of WSNs did not change the mesopore structure of WSNs, we determined that the removal efficiencies of the surface-modified WSNs for BTEX were considerably affected by the surface characteristics of the adsorbents. HDTMS-WSNs outperformed the other adsorbents in this study. In particular, the removal efficiencies of HDTMS-WSNs with long alkyl chains for BTEX in air were higher than that of OTES-WSNs because the dispersion forces between BTEX and HDTMS-WSNs were stronger than those between BTEX and OTES-WSNs.

SE-WSNs present a wide range of industrial applications. However, we

believe that surface modification of mesoporous silica can expand its potential applications to adsorbents for the removal of specific indoor air pollutants. Moreover, we believe that mesoporous silica can be used to purify indoor air with high concentrations of specific VOCs in excess of the typical background level (e.g. printing offices, building material factories, and electronic goods manufacturing plants). Furthermore, mesoporous silica can be used as a building material for sport facilities and filters in air cleaners.

5. References

- [1] Ninyà, N.; Vallecillos, L.; Marcé, R. M.; Borrull, F. Sci. Total Environ.
 2022, 836, 155611.
- [2] Domínguez-Amarillo, S.; Fernández-Agüera, J.; Cesteros-García, S.;
 González-Lezcano, R. A. Int. J. Environ. Res. Public Health 2020, 17, 7183.
- [3] Jiang, J.; Ding, X.; Isaacson, K. P.; Tasoglou, A.; Huber, H.; Shah, A.
 D.; Jung, N.; Boor, B. E. *J Hazard Mater Lett.* 2021, 2, 100042.
- [4] Fermo, P.; Artíñano, B.; De Gennaro, G.; Pantaleo, A. M.; Parente, A.; Battaglia, F.; Colicino, E.; Di Tanna, G.; Goncalves da Silva Junior, A.; Pereira, I. G.; Garcia, G. S.; Garcia Goncalves, L. M.; Comite, V.; Miani, A. *Experimental Results. Environ. Res.* 2021, 197, 111131.
- [5] Vardoulakis, S.; Giagloglou, E.; Steinle, S.; Davis, A.; Sleeuwenhoek,

A.; Galea, K. S.; Dixon, K.; Crawford, J. O. Int. J. Environ. Res. Public Health 2020, 17, 8972.

- [6] Pui, W. K.; Yusoff, R.; Aroua, M. K. Rev. Chem. Eng. 2019, 35, 649.
- [7] K. P. Veerapandian, S.; De Geyter, N.; Giraudon, J.-M.; Lamonier, J.-F.; Morent, R. *Catalysts* 2019, 9, 98.
- [8] Li, X.; Yuan, J.; Du, J.; Sui, H.; He, L. Ind. Eng. Chem. Res. 2020, 59, 3511.
- [9] Liu, C.; Cai, W.; Liu, L. Appl. Clay Sci. 2018, 162, 113.
- [10] Lai, C.; Wang, Z.; Qin, L.; Fu, Y.; Li, B.; Zhang, M.; Liu, S.; Li, L.;
 Yi, H.; Liu, X.; Zhou, X.; An, N.; An, Z.; Shi, X.; Feng, C. Coord. Chem. Rev. 2021, 427, 213565.
- [11] Li, X.; Zhang, L.; Yang, Z.; Wang, P.; Yan, Y.; Ran, J. Sep. Purif. Technol. 2020, 235, 116213.
- [12] Zhu, L.; Shen, D.; Luo, K. H. J. Hazard. Mater. 2020, 389, 122102.
- [13] Chiang, Y.-C.; Chiang, P.-C.; Huang, C.-P. Carbon N. Y. 2001, 39, 523.
- [14] Zhang, W.; Li, G.; Yin, H.; Zhao, K.; Zhao, H.; An, T. Environ. Sci. Nano 2022, 9, 81.
- [15] Li, L.; Liu, S.; Liu, J. J. Hazard. Mater. 2011, 192, 683.
- [16] Du, Y.; Chen, H.; Xu, X.; Wang, C.; Zhou, F.; Zeng, Z.; Zhang, W.;
 Li, L. *Microporous Mesoporous Mater.* 2020, 293, 109831.
- [17] Soltani, R.; Marjani, A.; Shirazian, S. J. Hazard. Mater. 2019, 371, 146.
- [18] Palliyarayil, A.; Saini, H.; Vinayakumar, K.; Selvarajan, P.; Vinu, A.;

Kumar, N. S.; Sil, S. Emergent Mater. 2021, 4, 607.

- [19] Nakaoka, H.; Todaka, E.; Seto, H.; Saito, I.; Hanazato, M.; Watanabe,
 M.; Mori, C. *Indoor Built Environ.* 2014, 23, 804.
- [20] Mazzatenta, A.; Pokorski, M.; Di Giulio, C. Physiol. Rep. 2021, 9, e15034.
- [21] Hinwood, A. L.; Rodriguez, C.; Runnion, T.; Farrar, D.; Murray, F.; Horton, A.; Glass, D.; Sheppeard, V.; Edwards, J. W.; Denison, L.; Whitworth, T.; Eiser, C.; Bulsara, M.; Gillett, R. W.; Powell, J.; Lawson, S.; Weeks, I.; Galbally, I. *Chemosphere* 2007, 66, 533.
- [22] Yoon, J.-H.; Kwak, W. S.; Ahn, Y.-S. Ann. Occup. Environ. Med.2018, 30.
- [23] McMichael, A. J. IARC Sci. Publ. 1988, 85, 3.
- [24] Bari, M. A.; Kindzierski, W. B.; Wheeler, A. J.; Héroux, M.-È.;Wallace, L. A. Build. Environ. 2015, 90, 114.
- [25] Zhang, Y.; Mo, J.; Li, Y.; Sundell, J.; Wargocki, P.; Zhang, J.; Little, J. C.; Corsi, R.; Deng, Q.; Leung, M. H. K.; Fang, L.; Chen, W.; Li, J.; Sun, Y. Atmos. Environ. 2011, 45, 4329.
- [26] Moon, D.-S.; Lee, J.-K. Langmuir 2014, 30, 15574.
- [27] ISO 16017-1: Indoor, Ambient and Workplace Air Sampling and Analysis of Volatile Organic Compounds by Sorbent Tube/Thermal Desorption/Capillary Gas Chromatography - Part 1: Pumped Sampling; 2000.
- [28] Parida, S. K.; Dash, S.; Patel, S.; Mishra, B. K. Adv. Colloid Interface

Sci. 2006, 121, 77.

- [29] Odenwald, C.; Kickelbick, G. J. Solgel Sci. Technol. 2019, 89, 343.
- [30] Ou, D. L.; Seddon, A. B. J. Non Cryst. Solids 1997, 210, 187.
- [31] Llusar, M.; Monrós, G.; Roux, C.; Pozzo, J. L.; Sanchez, C. J. Mater. Chem. 2003, 13, 2505.
- [32] Brunauer, S.; Deming, L. S.; Deming, W. E.; Teller, E. J. Am. Chem. Soc. 1940, 62, 1723.
- [33] Sing, K. S. W. Pure Appl. Chem. 1985, 57, 603.
- [34] Bai, W.; Qian, M.; Li, Q.; Atkinson, S.; Tang, B.; Zhu, Y.; Wang, J. J. Environ. Chem. Eng. 2021, 9, 105793.
- [35] Kumar, K. V.; Gadipelli, S.; Wood, B.; Ramisetty, K. A.; Stewart, A. A.; Howard, C. A.; Brett, D. J. L.; Rodriguez-Reinoso, F. J. Mater. Chem. A Mater. Energy Sustain. 2019, 7, 10104.
- [36] Delle Site, A. J. Phys. Chem. Ref. Data 2001, 30, 187.
- [37] Coasne, B.; Pellenq, R. J.-M. J. Chem. Phys. 2004, 120, 2913.
- [38] Fujii, A.; Shibasaki, K.; Kazama, T.; Itaya, R.; Mikami, N.; Tsuzuki, S. Phys. Chem. Chem. Phys. 2008, 10, 2836.
- [39] Shibasaki, K.; Fujii, A.; Mikami, N.; Tsuzuki, S. J. Phys. Chem. A 2006, 110, 4397.
- [40] Sinnokrot, M. O.; Sherrill, C. D. J. Am. Chem. Soc. 2004, 126, 7690.
- [41] London, F. Trans. Faraday Soc. 1937, 33, 8b.
- [42] Areerob, T.; Grisdanurak, N.; Chiarakorn, S. Environ. Sci. Pollut. Res. Int. 2016, 23, 5538.

Chapter 3.

Surface Manipulation of Graphene Oxide for Removing Formaldehyde in Air

1. Introduction

Since the COVID-19 pandemic, the importance of managing indoor air pollutants has become more prominent because people spend a substantial proportion of their time in buildings. Among these numerous pollutants, formaldehyde could be found in every indoor spaces because building materials (e.g., wood-based panels, furniture, paints, sealants, adhesives) are release it continuously with considerable amounts.^[1] Due to this ubiquitous characteristic and its carcinogenic toxicity, WHO had selected formaldehyde as one of the nine pollutants that should be managed as important in terms of public health.^[2] In the report, indoor exposures of formaldehyde are the dominant contributor to personal exposures through inhalation and indoor concentrations may be high enough to cause adverse health effects. The lowest concentration reported to cause sensory irritation of the eyes in humans is 0.36 mg m⁻³ for 4 hours. Increases in eye blink frequency and conjunctival redness show up at 0.6 mg m⁻³, which is considered equal to the no observed adverse effect level (NOAEL). Such being the case, WHO established an indoor air guideline value for formaldehyde at 0.1 mg m⁻³ for preventing sensory irritation in the general population. Despite the fact that formaldehyde is such a toxic chemical, the only ways suggested by WHO were to use low-emitting building materials and products, avoid tobacco smoke, and do natural or mechanical ventilation frequently. Therefore, it is to develop another method that could efficiently remove valuable formaldehyde in indoor air.

To date, a lot of scientific approaches have been addressed on removing indoor airborne chemicals including formaldehyde, e.g., adsorption,^[3-6] catalytic oxidation,^[7-9] photodegradation,^[10-12] biodegradation,^[13,14] plasma,^[15-18] and incineration.^[19] Among these methods, adsorption has been regarded as one of the most promising choice for formaldehyde abatement due to its simplicity, no secondary pollutants, and energy savings.^[20] Furthermore the adsorption has another merits coming from the specific features of various adsorbents, e.g., high surface area, simple surface modification, robustness to regeneration, facial pore structure manipulation, and low cost.^[21] One of the most frequently used conventional adsorbents for formaldehyde might be activated carbon (AC).^[22-25] Although their low manufacturing cost, micropore structure, hydrophobic and organophilic characteristics make AC to used widely for water and air purification systems, small adsorption capacity and short breakthrough time are still unsatisfied points especially in dealing with small molecule even after some improvements through surface modifications or combination as composite materials.^[26] AC could well adsorb chemicals with a boiling point above 0 °C. Unlike other indoor volatile organic compounds (VOCs) that could successively be abated by porous materials via physical adsorption, formaldehyde could not easily be removed by pure sorbent media due to its relatively low boiling point (-19.3 °C) and high vapor pressure (3,883 mmHg at 25 °C).^[27] As a result, it is hard to achieve satisfactory adsorption efficiency using conventional adsorbents. Among the allotrope of carbon, graphene-based materials has been getting more attention

recently due to their unique properties, e.g., extremely large specific surface area (theoretical 2,630 m² g⁻¹), chemical stability, mechanical strength, thermal conductivity, etc.^[28] Until now, most of the application of using graphene-based nanomaterials with formaldehyde have been focused on developing a detecting sensor.^[29-31] Some researches reported formaldehyde removal using CNT-graphene composite^[32] and catalytic element (e.g., Pt, TiO₂, etc)^[33,34] doped graphene, however, there are still some limitations on graphene or graphene oxide materials itself such as low adsorption capacity and relatively complex synthetic procedure to be a competent adsorbent for formaldehyde.

Herein, three-dimensional nitrogen doped mesoporous graphenes (NMGs) were prepared in order to enhance the removal efficiency of gaseous formaldehyde and compared its adsorption capacity with pure mesoporous graphenes (MGs) in room temperature and humidity conditions.

2. Materials and Methods

2.1. Chemicals and instrumentation

Commercial graphite (< 20 μ m), triblock copolymer Pluronic P123 (EO₂₀PO₇₀EO₂₀, M_W = 5,800) were obtained from Sigma Aldrich. Ammonium hydroxide (NH₄OH) was purchased from DaeJung Chemicals. All chemicals used in experiments without further purification.

XRD patterns of MGs and NMGs were obtained by powder X-ray

diffractometer (XRD, Ultima IV, Rigaku) using Ni filtered Cu K α radiation ($\lambda = 1.5418$ Å) at 40 kV and 30 mA. Thermogravimetric analysis (TGA) data were collected using a STA6000 (PerkinElmer) system in the temperature range of 30–800 °C at a heating rate of 5 °C min⁻¹ in the condition of 20 mL min⁻¹ of N₂ gas flow rate. The temperature range was from 30 to 800 °C with a heating rate of 5 °C min⁻¹. The morphology of the samples were observed using an JSM-7100F (JEOL) field-emission scanning electron microscopy (FE-SEM) instrument. N₂ adsorption-desorption experiments were conducted using a Belsorp II (BEL Japan) instrument at liquid N₂ temperature (77 K), and the specific surface areas of the MGs and NMGs were estimated using the Brunauer-Emmett-Teller (BET) method. The element composition of nitrogen were determined by using XPS (K-alpha plus, Thermo Fisher Scientific) with an excitation source of Al K_{α} radiation (1.4866 keV).

2.2. Preparation of exfoliated graphene oxide (GO)

To prepare the MGs and NMGs, modified Hummer's method which is commonly used chemical process to obtain GO from commercial graphite powder was adopted in a initial step.^[36] The as-prepared GO (1.2 g) was dispersed in deionized water (120 mL) and sonicated in an ultrasound bath (Sonics, Vibra-Cell, 160 W) for 30 min. The sonicated solution was centrifuged at 3000 r.p.m for 10 min to separate between unexfoliated GO particles and exfoliated ones,

2.3. Preparation of MGs and NMGs via soft-template route

A schematic diagram of MGs and NMGs preparation is shown in Scheme 1. To give a function of mesoporosity, two dimensional exfoliated GO went through inorganic-polymer composite process via soft-template method. The commercial triblock copolymer Pluronic P123 was used as a building block to prepare three dimensional exfoliated GO and P123 rod-like micelle composite structure.^[36] Specifically, 120 mL of the exfoliated GO suspension (10 mg mL⁻¹) and 480 mL of P123 aqueous solution (200 mg mL⁻¹) were homogeneously mixed under vigorous stirring for 24 h to form the MGs. In the case of NMGs, 130 mL of ammonium hydroxide was added as a nitrogen source. And the mixture was transferred into 1 L Teflon-sealed stainless steel autoclave. The autoclave condition was maintained at 180 °C for 24 h. After finishing the autoclave process, the composite gel was washed with deionized water and ethanol. And the washed sample directly moved into a dry oven and kept at 60 °C for 12 h. Finally, three dimensional MGs and NMG were obtained after eliminating rod-like polymer micelles by calcination at 700 °C under Ar gas stream for 3 h.

2.4. Formaldehyde adsorption performance of the MGs and NMGs

Adsorption experimental apparatus was based on the international standard ISO 12219-5:2019^[37] and 16000-23:2018.^[38] Formaldehyde quantitative analysis was followed by ISO 16000-3:2022.^[39] As shown in Figure 1, 6 mg of MGs and NMGs were set in each static 20 L stainless steel chamber

(SUS304). The 20 L chambers were installed in a temperature-controlled climate chamber. Before setting up the chamber and the other parts were washed with distilled water twice and baked out in a drying oven at 260 $^{\circ}$ C to wipe out any pollutants on chamber surface.



Figure 1. The schematic diagram (a) and instrument system picture (b) of formaldehyde adsorption test.

To quantify the amount of adsorbed formaldehyde, 2 μ g of formaldehyde solution (1000 μ g mL⁻¹ in water, AccuStandard) was injected directly into three different chambers (MGs, NMGs, Control). The injected amount of adsorbate had been decided by considering theoretically estimated monolayer coverage of formaldehyde molecules on the entire surface of adsorbents.

Amount of formaldehyde (g) =
$$\frac{W_a \times SA_a}{SA_f}$$

where, W_a is an amount of adsorbents (g), SA_a is a surface area of adsorbent (m² g⁻¹), and SA_f is a surface area of a formaldehyde molecule.

The chambers were immediately air tightened and maintained at 25 °C, 30% or 60% relative humidity. During the adsorption test, the air in the chamber was continuously circulated by a small stainless steel fan rotating 200 r.p.m.

The air inside MGs, NMGs, and control chamber were sampled after 12 h. Formaldehyde in air was sampled for 5 min at a flow rate of 50 mL min⁻¹ in a 2,4-dinitrophenylhydrazine (DNPH) cartridge equipped with an ozone scrubber using an MP- Σ 100 KNII pump (SIBATA Co., Japan, accuracy: \pm 5%). Each DNPH cartridge was eluted with 5 mL of acetonitrile using a solid extraction vacuum manifold (Supelco), The extracted solutions were analyzed by high-performance liquid chromatography (HPLC, Ultimate 3000, Thermo Fisher Scientific) with a C18 column (150 mm × 4.6 mm × 5 µm, Restek). Acetonitrile and water were allowed to flow at a ratio of 70:30 and a rate of 1 mL min⁻¹; Formaldehyde was detected at a UV wavelength of 360 nm. Formaldehyde-2,4-DNPH solution (100 µg mL⁻¹ in acetonitrile, Sigma Aldrich) was used as a certified formaldehyde standard.

The concentrations of adsorbed formaldehyde were estimated by subtracting the concentration of formaldehyde in the MGs or NMGs chamber from the amount of formaldehyde in the control chamber. The percentages of adsorbed formaldehyde in each chamber were calculated as follows:

% formaldehyde adsorbed = $\frac{(C_c - C_a)}{C_c} \times 100$,

where, C_c is the concentration of formaldehyde in the control chamber and C_a is the concentration of fomaldehyde in the MGs or NMGs chamber.

3. Results and Discussion

3.1. Sample characterization

At a specific critical micelles concentration, poloxamer such as P123 form various types of micelles including rod-shape micelles like hydrocarbon surfactants. The rod-like P123 polymers in this study were expected to act as a key material for enhancing formaldehyde adsorption capacity. Because of inter-layer π - π and van der Waals interactions, the graphene powder can not help reducing the number of functional groups available for formaldehyde adsorption to lower the adsorption efficiency. Thus, to overcome this limitation, polymer-supported graphene sheets were applied to reduce the aggregation and restacking effect and to make more sites available for adsorption.

To make sure the MGs and NMGs have been successfully synthesized via the soft-template method, several structural analyses were conducted. Main purposes of sample characterization were to confirm 1) the generation of mesoporosity, 2) the existence of n-doping sites on NMGs.



Figure 2. FE-SEM images for (a, b) MGs and (c, d) NMGs.

Figure 2 shows the FE-SEM images of MGs and NMGs. In low magnification images, the particle surfaces of all samples were not smooth, but wrinkled or crumpled. In addition, countless small pores were observed on the external surface of particles in higher magnification images. This highly open porous architecture could be one of clues that rod-like P123 micelles had been embedded between graphene nanosheets.



Figure 3. Powder X-ray diffraction patterns for (a) GO (b) MGs (c) NMGs.

The X-ray diffraction patterns of samples were shown in Figure 3. The symbolic diffraction peaks at $2\theta = 12.2^{\circ}$ were assigned to the (002) plane of GO with a *d*-spacing of 0.73 nm. On the other hand, MGs and NMGs showed relatively weak and broad diffraction peaks at $2\theta = 25.9^{\circ}$ with a *d*-spacing of 0.34 nm. This shrinkage of interlayer space ($\Delta = 0.39$ nm) resulted from the loss of oxygen functional groups on the surface of GO nanosheets. From the first-order reflection of a X-ray beam from the (002) plane of samples, the interplanar spacing, the spacing between adjacent (*hkl*) lattice planes, was estimated by Bragg's law.

The (10) diffraction peaks at $2\theta = 42.7^{\circ}$ (GO) and $2\theta = 43.1^{\circ}$ (MGs and NMGs), indicating a short range order in stacked graphene layers. When it comes to considering the full width at half maximum (FWHM) of (10) diffraction peaks, the FWHM of GO was much narrower than that of MGs and NMGs. It would be evidence that GO is more ordered than MGs and NMGs because the FWHM represents the order of the solid. It means that GO nanosheets had been exfoliated intentionally however a part of the nanosheets were restacked by cohesive effect, resulting in relatively higher crystallinity. On the other hand, the stacks of graphene layers of MGs and NMGs were randomly stick on the surface of P123 micelle rods and interrupting self-restacking of graphene nanosheets, resulting in showing relatively lower crystallinity and turbostratic disorder structure.^[40]

The Scherrer's equation with a constant equal to 0.91 was applied to (002) reflection for evaluating the average height of stacking layers, denoted as H. And Warren constant of 1.84 was applied to two dimensional (10) reflection for estimating the average diameter of stacking layers, denoted as D. The full widths were measured at the half maximum of the peak position of 002 and 10 bands to calculate the L_C , mean size of crystal in the *c*-direction and L_a , mean size of crystal in the *a*-direction (layer diameter), using Scherrer formula.

$$L = \frac{K \cdot \lambda}{B_{2\theta} \cos \theta}$$

where, λ is the wavelength of X-ray used (0.15418 nm), $B_{2\theta}$ is the full widths and K, a constant which was 0.91 and 1.84 for L_C and L_a calculation, respectively. The average number of layers per GO stack for Scherrer's approach,

$$n = \frac{Lc}{d}$$

Table 1 showed the comparison of structural parameters which were estimated by above equations.^[41] The GO consists of 5~6 graphene layers spacing 0.73 nm apart from each other in a stacking nanostructure of an average diameter by height of about 12.9 nm \times 4 nm. About 4 graphene layers spacing 0.34 nm were located in a 6.78 nm \times 1.22 nm sized stacking block of MGs. And similarly, a 5.83 nm \times 1.15 nm sized NMGs stacking block consisted of about 3 graphene nanosheets spacing 0.34 nm distance (Scheme 1). Addition of ammonium hydroxide for nitrogen doping did not have any influence on the interlayer spacing, but the crystal size, number of nanosheets in a stack, and crystallinity. The pore structure of samples were investigated by N₂ adsorption-desorption isotherms (Figure 4) and their results were summarized in Table 2. All sample showed hybrid type of I(a) an VI(a) isotherms according to IUPAC classification.^[42]

Sample	Peak (002)				Peak (10)			
	2θ (deg)	FWHM (deg)	H (nm)	<i>d</i> (nm)	n	2θ (deg)	FWHM (deg)	D (nm)
GO	12.2	1.99	4.04	0.73	5.6	42.7	1.26	12.9
MGs	25.9	6.66	1.22	0.34	3.5	43.1	2.40	6.78
NMGs	25.9	7.04	1.15	0.34	3.3	43.1	2.79	5.83

Table 1. Comparison of Structural Parameters of GO, MGs, and NMGs Resulting from the XRD Patterns.

Scheme 1. Schematic Diagram of MGs and NMGs Which Is Reflected Their Structural Parameters.



It suggested that they had both characteristics of microporous solids and mesoporous solids. And the outer shapes of MGs and NMGs could be assumed to be large monolithic particles having no interparticular porosity since isotherms showed small capillary condensations of nitrogen at high partial pressure. The hysteresis loop of all samples exhibited a typical H2(a) type attributed either to pore-blocking/percolation in a narrow range of pore necks or to cavitation-induced evaporation. The ink-bottle pore shape, features of type H2(a) hysteresis, would be induced from a partial deformation of the end of cylindrical P123 micelles by washing with ethanol and water in the process. The BET specific surface areas were 950 and 1108 $m^2\ g^{\text{-1}}$ for MGs and NMGs, with a total volume of pores of 1.70 and 1.40 mL g⁻¹, with a mean pore diameter of 7.16 and 5.06 nm, respectively. The features of mesopore structure showed significant differences between MGs and NMGs rather than that of total pore structures. The decrease in mean mesopore diameter and the increase in specific surface area sample came from the smaller dimension of NMGs stacking units than that of MGs. This is also consistent with previous XRD results.

Sample	S_{BET} (m ² g ⁻¹)	Pore volume (mL g ⁻¹)			Pore diameter (nm)	
		V_t^{a}	$V_m{}^{\rm b}$	V_m/V_t	D_t^{c}	$D_m{}^{\mathrm{d}}$
MGs	950	1.70	1.51	0.89	7.16	11.22
NMGs	1108	1.40	1.19	0.85	5.06	6.44

Table 2. Comparison of Pore Structure Parameters of MGs and NMGs.

^a The total pore volume at $P/P_0 = 0.99$; ^b The mesopore volume (BJH); ^c The mean pore diameter; ^d The average mesopore diameter (BJH)



Figure 4. (a) Nitrogen adsorption-desorption isotherms and (b) BJH pore size distribution of MGs and NMGs.



Figure 5. FE-SEM images and EDS maps of NMGs.

From the elemental mapping of EDS, the distribution nitrogen in NMGs was revealed to be homogeneous (Figure 5). The mapping images implied that nitrogen atoms were well doped on every basal plane of graphene nanosheets regularly by reaction between GO and NH₄OH. Figure 6(a) showed XPS survey spectra of MGs and NMGs in the range of 200-700 eV. In the MGs sample, the carbon and oxygen were detected at 285 and 532 eV, respectively. On the other hand, a notable N 1s peak was monitored at 399 eV in the NMGs sample. The overall nitrogen atomic percentages of NMGs was determined to be about 6 at %. Various nitrogen components in NMGs were further analyzed by fitting high-resolution N 1s spectra as shown in Figure 6(b).



Figure 6. (a) XPS survey specra of MGs and NMGs (b) high-resolution N 1s spectra of NMGs.

Deconvolution of the N 1s line scan revealed the present of pyridinic-N (N-6, 398.5 eV), pyrrolic-N (N-5, 400.1 eV), graphitic-N (N-Q, 401.5 eV) and pyridinic-N-oxide (N-O, 404.0 eV). From the peak intensity, the proportion of nitrogen contents were 41.7% (N-6), 30% (N-5), 21.7% (N-Q) and 6.7% (N-O).

The most abundant N-6 species were generated by the substitution of one carbon atom in a C_6 ring by one nitrogen atom with two sp^2 bonds. According to the reactivity of N-functional groups, the N-6 and N-5 mainly acted as adsorption sites for improving the gas adsorption.

3.2. Formaldehyde Adsorption capacity of MGs and NMGs

Figure 7 showed the formaldehyde adsorption capacities of MGs and NMGs at 25 °C with different relative humidity conditions. Average

adsorption efficiencies of MGs and NMGs at RH 30% were 42.7% and 85.8%. The mean adsorption performances of MGs and NMGs at RH 60% were 33.9% and 44.3%.



Figure 7. Adsorption capacity of MGs and NMGs for formaldehyde in air.

The resulting n-doping mesoporous graphenes exhibited better adsorption efficiency than the original mesoporous graphenes. There are several factors that can affect the performance of a porous inorganic material for gas adsorption. These include the specific surface area, the porosity, the chemical composition of the materials, the temperature, humidity and pressure at which the gas is adsorbed, and the type of gas being adsorbed. Because the gap of specific surface areas between two adsorbents was small about 15%, this large difference might be explained by the other affecting factors. Compared with pristine graphite, the improved performance of NMGs for formaldehyde uptake is attributed to the synergistic effect of physisorption (contributed by micropore structure) and chemisorption (contributed by surface functional group). The carbonyl group of a formaldehyde molecule could react with an amino group and finally an imine group is formed as a result.^[43]

 Table 3. Density Functional Theory (DFT) Calculation Results between

 N-Doping Graphene and Formaldehyde.^[44]

Functional group	Control (Pristine)	pyridinic-N (N-6)	pyrrolic-N (N-5)
$E_{ads}{}^a$	-0.07652	-0.15359	-0.41246
Optimal Geometry ^b			
Functional group	graphitic-N (N-Q)	pyridinic-N-oxide (N-C))
Eads	-0.24172	-0.18524	
Optimal Geometry			C C C N

^a theoretical adsorption energy for the most stable formaldehyde adsorption configuration; ^b optimal geometry of functional groups upon formaldehyde adsorption

As demonstrated in Table 3, Su et al. conducted theoretical calculation by using density functional theory (DFT) for relationship between formaldehyde gas and n-doping graphene under dried air condition.^[44] The adsorption energy (-0.07652 eV) of pristine graphene was significantly lower than that of n-doping graphenes. Among the n-doping graphene, the pyrrolic-N (N-5) graphene was energetically favorable for formaldehyde removal (-0.41246 eV). In a dried air condition, the total adsorption energy (-0.25265 eV) of NMGs for formaldehyde could be estimated in Table 4 combining the results of high-resolution N 1s spectra of NMGs. This interaction force is 3.3 times stronger than the pristine carbon materials.

Table 4. Estimated Adsorption Energy of NMGs for FormaldehydeCombining the Results from the DFT Calculation and High-Resolution N 1sXPS Spectra.

	N-6	N-5	N-Q	N-O
E_{ads} (eV)	-0.15359	-0.41246	-0.24172	-0.18524
$\mathbf{P}_n (\%)^a$	41.7	30.0	21.7	6.7
Adjusted E_{ads} (eV)	-0.06405	-0.12374	-0.05245	-0.01241
Total E_{ads} (eV)	-0.25265			

^a proportion of nitrogen contents which was estimated by XPS spectra.

The adsorption performances of MGs dropped slightly, while that of NMGs sharply fell by about 50% in the high humidity condition. It is already known that the relative humidity does not have critical effect on adsorption performance for physisorption unless it is over 70~80%.^[45] However, for chemical adsorption of formaldehyde, the water vapor effect

may be different due to the water solubility of formaldehyde, different reaction mechanisms, and competition with other adsorbate for occupying the limited active sites on the surface of base media. Therefore, water vapor has a negative effect on some chemisorbent materials and it was also applied in this study. Although the 60% RH condition did not affect physisorption which was contributed by micropore structures, the force of chemisorption severely influenced this negative effect.

4. Conclusions

Mesoporous graphene oxide was synthesized *via* a soft-templated method using P123 polymers. A portion of their surface carbon atoms were homogeneously exchanged with nitrogen atoms about 6 at %.

The variation range of relative humidity in common indoor space is from 20 to 80%. Although there is a difference depending on the relative humidity, NMG shows the dramatic formaldehyde in air with 85.8-44.3%. Among the critical factors affecting formaldehyde adsorption, the adsorbate-adsorbent interaction energy and specific surface areas.

Graphene oxide presents a variety of industrial applications. However, we believe that the pathway to build a robust 3D structure and surface modification can expand its potential applications to adsorbents for the removal of specific indoor air pollutants. Moreover, we believe that NMGs can be used to purify indoor air with high concentrations (e.g., workplace in building materials production line (paints, adhesive, wood-based panel, sealant, spay, etc.)).

5. References

- [1] Salthammer, T.; Mentese, S.; Marutzky, R. Chem. Rev. 2010, 110, 2536.
- [2] *WHO guidelines for indoor air quality: selected pollutants.* Who.int. https://www.who.int/publications/i/item/9789289002134 (accessed 2022-12-02).
- [3] Na, C.-J.; Yoo, M.-J.; Tsang, D. C. W.; Kim, H. W.; Kim, K.-H. J. Hazard. Mater. 2019, 366, 452.
- [4] Krishnamurthy, A.; Thakkar, H.; Rownaghi, A. A.; Rezaei, F. Ind. Eng. Chem. Res. 2018, 57, 12916.
- [5] de Falco, G.; Li, W.; Cimino, S.; Bandosz, T. J. Carbon N. Y. 2018, 138, 283.
- [6] Zhao, X.; Chen, L.; Guo, Y.; Ma, X.; Li, Z.; Ying, W.; Peng, X. Appl. Mater. Today 2019, 14, 96.
- [7] Miao, L.; Wang, J.; Zhang, P. Appl. Surf. Sci. 2019, 466, 441.
- [8] Dai, Z.; Zhu, J.; Yan, J.; Su, J.; Gao, Y.; Zhang, X.; Ke, Q.; Parsons,
 G. N. Adv. Funct. Mater. 2020, 30, 2001488.
- [9] Wang, H.; Guo, W.; Jiang, Z.; Yang, R.; Jiang, Z.; Pan, Y.; Shangguan,
 W. J. Catal. 2018, 361, 370.
- [10] Xia, S.; Zhang, G.; Meng, Y.; Yang, C.; Ni, Z.; Hu, J. Appl. Catal. B
 2020, 278, 119266.
- [11] Wu, Q.; Ye, J.; Qiao, W.; Li, Y.; Niemantsverdriet, J. W. (hans);
 Richards, E.; Pan, F.; Su, R. Appl. Catal. B 2021, 291, 120118.
- [12] Sahrin, N. T.; Nawaz, R.; Fai Kait, C.; Lee, S. L.; Wirzal, M. D. H. Nanomaterials 2020, 10, 128.
- [13] Yang, Z.; Miao, H.; Rui, Z.; Ji, H. Polymers 2019, 11, 276.
- [14] Chen, Q.; Liu, L. J. Environ. Chem. Eng. 2020, 8, 104143.

- [15] Zheng, Q.; Sun, T.; Fang, L.; Zheng, L.; Li, H. Nano Energy 2022, 102, 107706.
- [16] Asilevi, P. J.; Boakye, P.; Oduro-Kwarteng, S.; Fei-Baffoe, B.; Sokama-Neuyam, Y. A. Sci. Rep. 2021, 11, 22830.
- [17] Chang, T.; Shen, Z.; Ma, C.; Lu, J.; Huang, Y.; Veerapandian, S. K.
 P.; De Geyter, N.; Morent, R. J. Environ. Chem. Eng. 2021, 9, 105773.
- [18] Zhu, B.; Zhang, L.-Y.; Li, M.; Yan, Y.; Zhang, X.-M.; Zhu, Y.-M. Chem. Eng. J. 2020, 381, 122599.
- [19] Tessitore, J. L. Control of VOCs by Incineration. In Sizing and Selecting Air Pollution Control Systems; CRC Press: Boca Raton, FL, 2020; pp 117-129.
- [20] Suresh, S.; Bandosz, T. J. Carbon 2018, 137, 207.
- [21] Robert, B.; Nallathambi, G. Environ. Chem. Lett. 2021, 19, 2551.
- [22] Chang, S.-M.; Hu, S.-C.; Shiue, A.; Lee, P.-Y.; Leggett, G. Chem. Phys. Lett. 2020, 757, 137864.
- [23] Isinkaralar, K.; Gullu, G.; Turkyilmaz, A. Biomass Convers. Biorefin.2022, 464.
- [24] Zhang, D.; Zhang, M.; Ding, F.; Liu, W.; Zhang, L.; Cui, L. Environ. Sci. Pollut. Res. Int. 2020, 27, 18109.
- [25] Ryu, D.-Y.; Shimohara, T.; Nakabayashi, K.; Miyawaki, J.; Park, J.-I.; Yoon, S.-H. J. Ind. Eng. Chem. 2019, 80, 98.
- [26) Kumar, V.; Kumar, S.; Kim, K.-H.; Tsang, D. C. W.; Lee, S.-S. Environ. Res. 2019, 168, 336.
- [27] Hu, S.-C.; Chen, Y.-C.; Lin, X.-Z.; Shiue, A.; Huang, P.-H.; Chen,
Y.-C.; Chang, S.-M.; Tseng, C.-H.; Zhou, B. Environ. Sci. Pollut. Res. Int. 2018, 25, 28525.

- [28] Tiwari, S. K.; Sahoo, S.; Wang, N.; Huczko, A. J. Sci. Adv. Mater. Devices 2020, 5, 10.
- [29] Hu, J.; Chen, M.; Rong, Q.; Zhang, Y.; Wang, H.; Zhang, D.; Zhao, X.; Zhou, S.; Zi, B.; Zhao, J.; Zhang, J.; Zhu, Z.; Liu, Q. Actuators B Chem. 2020, 307, 127584.
- [30] Kumar, V.; Vikrant, K.; Kim, K.-H. Trends Analyt. Chem. 2019, 121, 115694.
- [31] Fan, J.; Li, H.; Hu, H.; Niu, Y.; Hao, R.; Umar, A.; Al-Assiri, M. S.;
 Alsaiari, M. A.; Wang, Y. *Microchem. J.* 2021, 160, 105607.
- [32] Wu, L.; Qin, Z.; Zhang, L.; Meng, T.; Yu, F.; Ma, J. New J Chem 2017, 41, 2527.
- [33] Yu, L.; Wang, L.; Sun, X.; Ye, D. J. Environ. Sci. 2018, 73, 138.
- [34] Yan, Z.; Xu, Z.; Yang, Z.; Yue, L.; Huang, L. Appl. Surf. Sci. 2019, 467, 277
- [35] Hummers, W. S.; Offeman, R. E. J. Am Chem Soc 1958, 80, 1339.
- [36] Luo, H.; Jiang, K.; Liang, X.; Hua, C.; Li, Y.; Liu, H. Colloids Surf. A Physicochem. Eng. Asp. 2019, 572, 221.
- [37] *ISO 12219-5:2014.* ISO. https://www.iso.org/standard/56876.html (accessed 2022-12-13).
- [38] ISO 16000-23:2018. ISO. https://www.iso.org/standard/70809.html (accessed 2022-12-13).
- [39] ISO 16000-3:2022. ISO. https://www.iso.org/standard/81864.html (accessed 2022-12-13).

- [40] Liu, K.; Lu, F.; Li, K.; Xu, Y.; Ma, C. Appl. Surf. Sci. 2019, 493, 1255.
- [41] Sharma, A.; Kyotani, T.; Tomita, A. Carbon 2000, 38, 1977.
- [42] Donohue, M. D.; Aranovich, G. L. Adv. Colloid Interface Sci. 1998, 76.
- [43] Zhang, S.; Yang, Q.; Zhou, X.; Li, Z.; Wang, W.; Zang, X.; Wang, C.; Shiddiky, M. J. A.; Murugulla, A. C.; Nguyen, N.-T.; Wang, Z.; Yamauchi, Y. Analyst 2018, 144, 342.
- [44] Su, C.; Liu, K.; Zhu, J.; Chen, H.; Li, H.; Zeng, Z.; Li, L. Chem. Eng. J. 2020, 393, 124729.
- [45] Cal, M. P.; Rood, M. J.; Larson, S. M. Gas sep. purif. 1996, 10, 117.

Chapter 4.

Indoor Air Pollutants and Their Risk Assessments

Part I. Prevalence of sick building syndrome symptoms and subjective-objective indoor air quality of stores in underground shopping districts of Korea

* This chapter is slightly modified version of the article:

Shim, I.-K.; Kim, J.; Won, S. R.; Hwang, E. S.; Lee, Y.; Park, S.; Ryu, J.; Lee, J. Build. Environ. 2023, 228(109882), 109882. http://doi.org/10.1016/j.buildenv.2022.109882

1. Introduction

Sick building syndrome (SBS) encompasses symptoms associated with the indoor environments of office occupants, including irritation of the upper respiratory tract (e.g., nose or throat), eyes, and skin, as well as headache and fatigue.^[1,2] Notably, these symptoms are related to both environmental and individual characteristics; the former include indoor air pollution (e.g., volatile organic compounds—VOCs), biological airborne contaminants,^[3,4] and building characteristics (e.g., inadequate ventilation or dampness)^[5,6] and the latter includes sex, age, history of allergies, psychosocial work stress, depression, and anxiety.^[2,7,8] For indoor air quality (IAQ), formaldehyde and VOC concentrations have been found as causative factors in SBS.^[9,10] However, a clinical definition has not been confirmed, and no definitive pathological theory of pathogenic etiology has been put forth since SBS was defined by a WHO in 1983.^[1,11]

Subjective IAQ perception, including perceived odor and sensory effects, is commonly associated with VOCs and other air contaminants.^[12] Indoor odorants include human body odors, tobacco smoke, VOCs from building materials, perfumes, air fresheners, and bio-odorants (e.g., mold and animal-derived materials).^[13] Simultaneously, sensory inflammation of the eyes and upper respiratory tracts may be caused by airborne chemicals irritating the mucosa or skin,^[14,15] often being described as "dryness".^[16,17] The relationship between the prevalence of SBS symptoms and occupants'perceived IAQ have been conducted in offices, homes, and hospitals;^[8,17-20] but, few studies have been conducted on workers in underground space.^[21,22]

The use of underground spaces is increasing worldwide for many purposes, such as transportation and commercial facilities.^[23] However, IAQ of such underground spaces can be worse than aboveground equivalents owing to poorer ventilation capacities (e.g., difficulty in incorporating natural ventilation) under such structural constraints. One previous study conducted in large department store buildings reported that CO₂, formaldehyde, and total VOC (TVOC) concentrations were higher in underground spaces than those aboveground.^[24] Particularly, underground shopping districts (USDs) are often crowded by passengers, shoppers, and employees in urban areas, there are numerous potential sources of indoor air pollution from transportation and commercial facilities. To manage USD IAQ, the Korean government regulates USDs with a net floor area of $\geq 2000 \text{ m}^2$ based on the Indoor Air Quality Management Act, which managed 64 USDs in 2018.^[25] Nevertheless, in comparison to passengers or shoppers, USD store workers incur a significantly greater exposure duration. Kim et al. investigated the prevalence of SBS symptoms in USDs and their relationships with the perceived IAQ perceptions of store workers, revealing that approximately half of store workers had experienced SBS symptoms and that perceived IAQ is associated with SBS symptoms (adjusted odds ratios, aOR = 1.81-7.84);^[22] however, information on their relationships with environmental IAQ monitoring data in USDs is limited. Accordingly, the purpose of this study was to determine the relationships among SBS symptoms, IAQ perception, and indoor aldehyde and VOC concentrations in USD stores. Both subjective and objective IAQ measurements at the USD working-area level were used to examine correlated factors associated with SBS symptoms.

2. Material and Methods

2.1 Participants

In 2020, 25 USDs existed in Seoul. Using general status data from USD stores in Seoul in 2020 [26], we aimed to collect data from 500 of the 2,788 stores in the 25 USDs. Trained interviewers without prior knowledge visited the USD stores between June and October (mostly in the summer season). Stores were selected if they had at least one worker > 20 years of age, who worked > 6 months at the location, for \geq 8 h day⁻¹. The store categories, which included clothing, fashion accessory (e.g., shoe or luggage shops), and food (e.g., restaurants, bakeries, or cafes), were also considered to include similar proportions of different store types. Store workers were then asked to complete a computer-assisted personal interview using tablet computers. Across the 25 USDs, one was remodeling and another was not operating; thus, 454 stores across 23 USDs participated in the study.

Here, 10 of the 23 USDs were selected for objective IAQ measurement, including aldehyde compounds and VOC concentrations in stores. Across these 10 USDs, the net floor areas ranged from 2,997–31,566 m², and the number of participating stores ranged from 5 to 27. All USDs are operated with heating, ventilation, and air conditioning systems under normal conditions. During the personal interviews,the interviewers asked store workers to participate in IAQ measurements. Ultimately, 128 stores across the 10 USDs were included in this analysis. We obtained IAQ measurements upon visitation within 2 weeks of the personal interviews with store workers.

2.2 Questionnaires

Information on demographic and job characteristics, SBS symptoms, and subjective IAQ perception was included in the questionnaires. Demographic details included sex, age, education level, current smoking status, and any medical diagnoses of allergies, whereas job characteristics included the type of store, working period, working hours, and door status of participants' stores (open or closed).

To examine subjective IAQ perception on SBS status, the same questions as in a previous study were applied,^[17] where 16 SBS questions based on a modified version of the National Institute for Occupational Safety and Health Indoor Air Quality and Work Environment Survey were provided. Specifically, the SBS questions were: "Have you experienced the following symptoms while working in your stores in the USDs in the last month?," where the participants chose one of the following options for each SBS symptom: "never," "neutral," "sometimes," and "frequently." All responses of "sometimes" or "frequently" were defined here as the presence of SBS. Furthermore, 16 SBS symptoms were categorized into four SBS groups, namely skin, eye irritation, respiratory, and general symptoms, based on clinical symptom characteristics.

For subjective IAQ, seven IAQ perception questions were used that have been previously applied as a qualitative index of IAQ.^[20,22] Specifically, the IAQ perception questions were "Have you experienced the following perception while working in your stores in the USD within the last month: (1) stuffy odor; (2) unpleasant odor; (3) pungent odor; (4) moldy odor; (5)

tobacco smoke odor; (6) humid air; or (7) dry air?," where a five-point scale was used: "never," "rarely," "neutral," "sometimes," and "frequently," and responses of "sometimes" or "frequently" were defined as "yes". The seven IAQ perceptions were categorized into two groups: "with" and "without," where if at least one of the seven IAQ perceptions was reported, the participant was considered to have IAQ perception.

2.3 Environmental monitoring

As most USDs are open from 10:00 to 22:00, all sampling was conducted for 30 min between 11:00 AM and 16:30 PM on weekdays under normal operating conditions. Measurement points were set at least 1 m away from the walls and 1.2–1.5 m above the floor, as central in the store as possible.

Parameters of temperature, relative humidity (RH), CO₂, 15 aldehyde compounds, and 42 VOCs were measured at the same time in each store for 30 min, and the averages of these individual measurements were used. Temperature (range, 0–60 °C; accuracy, \pm 0.6 °C), RH (range, 5–95% RH; accuracy, \pm 3.0% RH), and CO₂ concentrations (range, 0–5000 ppm; accuracy, \pm 3.0% of readings or \pm 50 ppm) were measured using an IAQ-CALC Model 7545 (TSI; Shoreview, MN, USA), whereas aldehydes and VOCs were measured according to the environmental standard method of the Korean Ministry of Environment. Aldehyde compounds were measured twice for 30 min at a flow rate of 500 mL min⁻¹ in a 2,4-dinitrophenylhydrazine (DNPH) cartridge equipped with an ozone scrubber using an MP- Σ 100 KNII pump (SIBATA Co., Japan, accuracy: \pm 5%). For VOCs, two samples were collected using a Tenax-TA (Supelco

Inc., Bellefonte, PA, USA) for 30 min at a flow rate of 100 mL min⁻¹ using an MP- Σ 30 KNII pump (SIBATA Co., accuracy: ± 5%). Aldehyde and VOC samples were sealed and stored below 4 °C until analysis.

During laboratory analysis, each DNPH cartridge was eluted with 5 mL of acetonitrile using a solid extraction vacuum manifold (Supelco), and the extracted solutions were analyzed using high-performance liquid chromatography (HPLC, Ultimate 3000, Thermo Fisher Scientific, Waltham, MA, USA) with a C18 column (150 mm \times 4.6 mm \times 5 μ m, Restek, Centre County, PA, USA). Acetonitrile and water were allowed to flow at a ratio of 70:30 and a rate of 1 mL min⁻¹; aldehyde compounds were detected at a UV wavelength of 360 nm. A TO11/IP-6A aldehyde/ketone-DNPH Mix solution (15 µg mL⁻¹; Supelco) was used as the standard. Method detection limits (MDLs) ranged from 0.14 μ g m⁻³ (formaldehyde) to 1.23 μ g m⁻³ (p-tolualdehyde) for the 15 aldehyde compounds.

VOCs adsorbed by Tenax-TA were analyzed using gas chromatography/mass spectrometry (GC/MS, Clarus 690/Clarus SQ8, PerkinElmer, Waltham, MA, USA). Tenax-TA tubes were desorbed at 280 °C for 15 min by thermal desorption (TD, TurboMatrix 650 ATD, PerkinElmer) and transported to a gas chromatograph with a VB-1 column (60 m \times 0.25 mm \times 1.0 μm). TVOC concentrations were estimated by summing the peaks from *n*-hexane to *n*-hexadecane, calculated using toluene calibration factors. Detailed TD-GC/MS analytical conditions are shown in Table 1.

Parar	neter	Conditions					
TD	Desorption time and flow	15 min, 60 mL min ⁻¹					
	Desorption temperature	280 °C					
	Cold trap packing	Tenax-TA					
	Trap cool temperature	−20 °C					
	In split	No					
	GC column	VB-1 (60 m \times 0.25 mm \times 1.0 μ m)					
	Initial temperature	40 °C (6 min)					
CC	Oven ramp rate 1	4 °C min ⁻¹ (40–180 °C)					
GC/	Oven ramp rate 2	20 °C min ⁻¹ (180–250 °C)					
1015	Final temperature	250 °C (10 min)					
	Column flow	1.5 mL min^{-1}					
	MS source temperature	200 °C					

Table 1. Thermal Desorption Gas Chromatography/Mass Spectrometry (TD-

GC/MS) Analytical Conditions.

All samples were calibrated and quantified using a 50 Component Indoor Air Standard (Supelco). MDLs ranged from 0.10 μ g m⁻³ (trichloroethylene) to 0.96 μ g m⁻³ (*n*-hexadecane) for the 42 VOCs.

The coefficient of determination (R²) for the calibration curve was > 0.999 for both the aldehyde compounds and VOCs. Concentrations of each aldehyde compound and VOCs < MDLs were assigned as $1/\sqrt{2}$ MDL. Detection frequencies > 90% for individual aldehyde compounds, VOCs, and TVOC were included in this study.

2.4 Statistical analyses

Univariable analyses of the relationships between the prevalence of SBS symptom groups and demographic or job characteristics of store workers were conducted using a chi-square test, whereas Spearman's correlations were used to examine the relationships among IAQ perception variables. The same correlations were used to examine the relationship between IAQ perception and temperature, RH, CO_2 , aldehyde compounds, and VOC concentrations. All individual IAQ substances measured at 128 stores were included in the statistical analysis. Because most aldehyde and VOC concentrations were log-normally distributed, concentrations are described using the geometric mean (GM) and geometric standard deviation (GSD), whereas temperature, RH, and CO_2 concentrations are described using the arithmetic mean (AM) and standard deviation (SD).

Multivariable logistic regression analysis was conducted to examine the relationships between the SBS symptom groups and IAQ perception. Sex, age, and the variables identified in the univariate analysis (p < 0.1) were included in the model. Although several SBS symptom groups were not associated with sex or age, they were included in the multivariable model for comprehensiveness. The same test was used to examine the relationships between SBS symptom groups and the individual concentrations of aldehydes or VOCs. Similarly, sex, age, and all variables identified in the univariate analysis (p < 0.1) were included. Environmental variables (temperature, RH, and CO₂) were selected using stepwise methods, whereas environmental IAQ monitoring data, including aldehyde compounds and VOCs, were used as the continuous variables. When the models examined SBS symptoms with benzene or decanal concentrations, RH was not used as a covariate, as it was significantly correlated between them (Pearson's r = 0.64 and 0.75, respectively). Similar criteria for the elimination of independent variables (r > |0.6|) in regression models have been used to avoid multicollinearity in previous studies.^[27,28] SAS (v.9.4, SAS Institute, Cary, NC, USA) was used for all statistical analyses, and p-values < 0.05 were set as significant.

3. Results

3.1 Prevalence of SBS symptom distribution

The prevalence of SBS symptoms in IAQ monitored store workers (n = 128) was similar to that in the non-IAQ monitored group(n = 326, Table 2).

 Table 2. Prevalence of SBS Symptoms in Underground Shopping District

 Store Workers.

		All	Non-IAQ monitored group (n=326, %)	IAQ monitored group (n=128, %)	<i>p</i> -value [*]
Skin	Skin dryness or itching	52 (11.5)	31 (9.5)	21 (16.4)	0.038
P	Dry, itching, or irritated eyes	137 (30.2)	97 (29.8)	40 (31.3)	0.755
Eye	Tired or stained eyes	96 (21.1)	65 (19.9)	31 (24.2)	0.315
irritation	Any eye irritation symptoms	175 (38.5)	125 (38.3)	50 (39.1)	0.887
	Stuffy or runny nose	40 (8.8)	28 (8.6)	12 (9.4)	0.790
	Cough	17 (3.7)	10 (3.1)	7 (5.5)	0.225
	Sneezing	51 (11.2)	29 (8.9)	22 (17.2)	0.012
Docningtom	Sore or dry throat	76 (16.7)	54 (16.6)	22 (17.2)	0.873
Kespiratory	Wheezing	16 (3.5)	13 (4)	3 (2.3)	0.393
	Shortness of breath or chest tightness	18 (4)	8 (2.5)	10 (7.8)	0.009
	Any respiratory symptoms	127 (28)	90 (27.6)	37 (28.9)	0.782
	Nausea or upset stomach	10 (2.2)	7 (2.1)	3 (2.3)	0.898
	Headache	68 (15)	45 (13.8)	23 (18)	0.263
	Tiredness, fatigue, or drowsiness	122 (26.9)	82 (25.2)	40 (31.3)	0.187
Comonal	Nervousness	61 (13.4)	42 (12.9)	19 (14.8)	0.582
General	Difficulty in remembering things or in concentrating	27 (5.9)	17 (5.2)	10 (7.8)	0.292
	Dizziness or lightheadedness	20 (4.4)	10 (3.1)	10 (7.8)	0.027
	Feeling depressed	17 (3.7)	12 (3.7)	5 (3.9)	0.909
	Any general symptoms	184 (40.5)	128 (39.3)	56 (43.8)	0.381

* Chi-square test

The majority of the 128 store workers were female (57.0%) and > 60 years old (39.8%). The distributions of the prevalence of 16 SBS symptoms and their symptom groups are listed in Figure 1. Within the SBS symptom group, the prevalence of skin, eye irritation, respiratory, and general symptoms was 16.4%, 39.1%, 28.9%, and 43.8%, respectively.

Univariate analysis of the prevalence of SBS symptom groups according to demographic and job characteristics is shown in Table 3. Several variables were correlated with prevalence of SBS symptom groups. The prevalence of skin symptoms was significantly higher in store workers with educational levels of "college or higher" than those of "high school or less" (p = 0.005), whereas that of general symptoms was marginally higher in store employees who worked > 8 h day⁻¹ than those who worked 8 h day⁻¹ (p = 0.080).





	T - 4 - 1	Ski	in	Eye irri	tation	Respir	atory	Gene	General	
	I otal	Yes (%)	p-value [*]	Yes (%)	p-value	Yes(%)	p-value	Yes (%)	p-value	
Demographic characteristics										
Sex										
Men	55	8 (14.5)	0.622	18 (32.7)	0.202	18 (32.7)	0.408	23 (41.8)	0.702	
Women	73	13 (17.8)		32 (43.8)		19 (26.0)		33 (45.2)		
Age(vr)		()		· · · ·		· · · ·		()		
<60	77	15 (19.5)	0.249	34 (44.2)	0.147	25 (32.5)	0.275	34 (44.2)	0.910	
≥ 60	51	6 (11.8)		16 (31.4)		12 (23.5)		22 (43.1)		
Education		()		· · · ·		()		()		
High school or less	66	5 (7.6)	0.005	24 (36.4)	0.519	16 (24.2)	0.230	26 (39.4)	0.305	
College or higher	62	16 (25.8)		26 (41.9)		21 (33.9)		30 (48.4)		
Current smoking status		- (/		- (-)		()				
No	104	15 (14.4)	0.207	40 (38.5)	0.772	29 (27.9)	0.596	48 (46.2)	0.254	
Yes	24	6 (25.0)		10(41.7)		8 (33.3)		8 (33.3)		
Doctor's diagnosis of allergy		· ()				• (•••••)		- (cere)		
No	109	17 (15.6)	0.553	44 (40.4)	0.469	32 (29.4)	0.787	48 (44.0)	0.876	
Yes	19	4 (21.1)		6 (31.6)		5 (26.3)		8 (42.1)		
Job characteristics		()		- ()		- (/		- ()		
Type of store										
Clothing	47	10 (21.3)	0.509	19 (40.4)	0.142	13 (27.7)	0.164	20 (42.6)	0.451	
Fashion accessories	41	6 (14.6)		20 (48.8)		16 (39.0)		21(51.2)		
Food service	40	5 (12.5)		11(27.5)		8 (20.0)		15(37.5)		
Working period(yr)		- ()		(_,,		- ()		(0,10)		
<4	29	6 (20.7)	0.106	8 (27.6)	0.143	6 (20.7)	0.670	11 (37.9)	0.536	
4-10	44	11 (25.0)		23(523)		15(341)		20 (45.5)		
11-20	30	2(6.7)		11(36.7)		9 (30.0)		16(53.3)		
>21	25	$\frac{2}{2}$ (8.0)		8 (32 0)		7 (28.0)		9 (36.0)		
$Working hours(h day^{-1})$	20	2 (0.0)		0 (0210)		, (2000)		, (2010)		
8	45	6 (13.3)	0.489	15 (33.3)	0.328	11 (24.4)	0.412	15 (33.3)	0.080	
>8	83	15 (18.1)		35 (42.2)		26 (31.3)		41 (49.4)		
Door open										
Open	5	2 (40.0)	0.146	2 (40.0)	0.965	2 (40.0)	0.577	2 (40.0)	0.863	
Semi-open	123	19 (15.4)		48 (39.0)		35 (28.5)		54 (43.9)		

Table 3. Distribution of SBS Symptom Prevalence by Demographic and Job Characteristics.

* Chi-square test

3.2 Perceived IAQ index and correlations

USD store workers mostly perceived dry or humid air (10.2%), followed by stuffy odors (5.5%), unpleasant, pungent, or tobacco smoke (3.9%), and moldy odors (1.6%). Among the seven IAQ perception indices, all were significantly correlated with each other, except between stuffy odors and humid air, pungent odors and dry and humid air, and tobacco smoke and humid air (Table 4).

3.3 Environmental monitoring data and IAQ perception

The indoor aldehyde compound and VOC concentrations of the 128 stores and their correlations with the categorized IAQ perceptions of workers in each store are shown in Table 5. IAQ perception was significantly correlated with RH (r = 0.26), formaldehyde concentration (r = 0.35), and benzene concentration (r = 0.24); however, temperature, CO₂, other aldehydes, VOCs, and TVOC concentrations were not significantly correlated with IAQ perception.

	Stuffy odor	Unpleasant odor	Pungent odor	Moldy odor	Tobacco smoke odor	Dry air	Humid air
Stuffy odor	1						
Unpleasant odor	0.48***	1.00					
Pungent odor	0.25**	0.62***	1.00				
Moldy odor	0.48***	0.58***	0.30***	1.00			
Tobacco smoke odor	0.34***	0.58***	0.46***	0.42***	1.00		
Dry air	0.49***	0.47***	0.17	0.47***	0.41***	1.00	
Humid air	0.15	0.20*	0.17	0.2*	0.11	0.32***	1.00

Table 4. Correlations among Perceived Indoor Air Quality Index.

* p < 0.05, ** p < 0.01, *** p < 0.001

Table 5. Indoor Aldehyde Compounds, VOC Concentrations (μ g m⁻³), and Their Correlations with Indoor Air Quality (IAQ) Perception of Workers of Stores in Underground Shopping Districts (USDs; n = 128).

		Mean	Spearman cor IAQ perc	relation of eption
		_	Rho	p-value
Temperature (°C)		$24.9~\pm~1.6$	-0.09	0.328
Relative humidity (%)	$AM\ \pm\ SD$	$51.8~\pm~14.8$	0.26	0.003
<i>CO</i> ₂ (ppm)		$822.0 \ \pm \ 191.4$	-0.05	0.608
Formaldehyde		27.4 (1.9)	0.35	< 0.001
Acetaldehyde		16.5 (1.9)	0.11	0.211
Propionaldehyde		1.7 (1.7)	0.07	0.433
Benzaldehyde		3.5 (1.9)	-0.15	0.089
Hexaldehyde		5.3 (1.7)	-0.04	0.629
Benzene		3.3 (2.0)	0.24	0.006
n-Butanol		1.6 (1.8)	-0.01	0.874
n-Heptane		2.9 (2.1)	0.16	0.065
Toluene		64.5 (2.7)	0.07	0.440
n-Butylacetate		2.7 (3.1)	0.12	0.196
n-Octane		2.4 (2.1)	0.05	0.540
Tetrachloroethylene	GM	0.5 (4.9)	0.07	0.460
Ethylbenzene	(GSD)	5.5 (2.1)	0.12	0.172
Xylene		9.9 (2.1)	0.15	0.102
Styrene		0.8 (1.9)	0.00	1.000
n-Nonane		1.1 (2.2)	0.16	0.064
1,4-dichlorobenzene		1.6 (2.6)	-0.01	0.930
D-Limonene		2.3 (2.4)	0.07	0.461
Nonanal		4.4 (1.9)	0.00	0.991
n-Undecane		1.0 (2.2)	0.12	0.174
Decanal		1.3 (1.8)	0.07	0.454
n-Dodecane		2.6 (3.1)	-0.03	0.711
n-Tetradecane		3.6 (2.1)	0.02	0.864
TVOC		288.3 (1.9)	0.06	0.509

IAQ = indoor air quality; AM = arithmetic means; SD = standard deviation; GM = geometric mean; GSD = geometric standard deviation; TVOC = total volatile organic compounds

3.4 SBS symptoms and LAQ perception

Figure 2 shows the multivariable logistic analysis of SBS symptom groups by categorized IAQ perception. Store workers who perceived IAQ were more likely to experience eye irritation (aOR = 4.00; 95% CI = 1.55-10.32) and respiratory (aOR = 4.71; 95% CI = 1.82-12.15) and general symptoms (aOR = 3.33; 95% CI = 1.32-8.42); however, skin symptom groups were not significantly associated with categorized IAQ perception.



**adjusted for sex, age

*** adjusted for sex, age, working hours



3.5 SBS symptoms and environmental monitoring data

Aldehyde compounds and VOC concentrations associated with SBS symptom groups in the univariate analysis (p < 0.1; Table 6) were examined using multivariable logistic regression analysis. After adjusting for demographic and job characteristics, as well as environmental factors selected by stepwise methods, store employees who worked in shops with higher concentrations of *n*-butanol (aOR = 1.37; 95% CI = 1.01-1.87), *n*-heptane (aOR = 1.25; 95% CI = 1.06-1.47), and xylene (aOR = 1.04, 95% CI = 1.01-1.08) were more likely to experience eye irritation symptoms (Figure 3). Moreover, workers in stores with higher concentrations of *n*-heptane (aOR = 1.13; 95% CI = 1.01-1.27) were more likely to experience respiratory symptoms and those in stores with higher concentrations of benzene (aOR = 1.17; 95% CI = 1.00-1.37), n-heptane (aOR = 1.24; 95% CI = 1.06-1.45), and decanal (aOR = 1.61; 95% CI =1.00-2.58) were more likely to experience general symptoms. Skin symptoms, however, were not significantly associated with any aldehydes or VOC concentrations.



***adjusted for sex, age, CO2

****adjusted for sex, age, working hours, relative humidity

*****adjusted for sex, age, working hours

******adjusted for sex, age, working hours, relative humidity, and CO2

Figure 3. Associations (aOR with 95% CI) between SBS symptom groups, aldehyde compounds and VOC concentrations (per μ g m⁻³). Demographic and job characteristic variables identified in the univariate analysis, sex, and age were included, and environmental variables (i.e., CO₂, temperature, and relative humidity) selected using stepwise methods were included in the multiple logistic regression model.

	_	Skin			Eye irritation			Respiratory			General		
		No(n=107)	Yes(n=21)	p-value*	No(n=78)	Yes(n=50)	p-value	No(n=91)	Yes(n=37)	p-value	No(n=72)	Yes(n=56)	p-value
Temperature (°C)	AM	$24.8~\pm~1.6$	$25.3~\pm~1.8$	0.213	$25.0~\pm~1.6$	$24.8~\pm~1.6$	0.551	$25.0~\pm~1.6$	$24.8~\pm~1.7$	0.562	$25.0~\pm~1.6$	$24.8~\pm~1.6$	0.380
RH (%)	±	$51.6~\pm~14.5$	52.4 ± 16.2	0.819	$51.8~\pm~14.3$	$51.6~\pm~15.6$	0.942	$51.4~\pm~15.3$	$52.7~\pm~13.4$	0.633	$48.9~\pm~16.4$	$55.4~\pm~11.4$	0.010
CO ₂ (ppm)	SD	$812.9\ \pm\ 194.8$	$868.4\ \pm\ 169.4$	0.226	$834~\pm~189.2$	$803.3\ \pm\ 195.1$	0.379	$820.1\ \pm\ 196.0$	826.8 ± 182.2	0.858	$820.9\ \pm\ 195.9$	823.4 ± 187.2	0.943
Formaldehdye		27.2 (1.9)	28.1 (1.9)	0.839	27.7 (1.9)	26.8 (1.8)	0.765	27.4 (1.9)	27.3 (1.8)	0.958	25.7 (2.0)	29.6 (1.7)	0.208
Acetaldehyde		16.1 (1.9)	18.9 (1.7)	0.300	16.9 (1.9)	15.9 (1.9)	0.596	16.2 (1.9)	17.3 (1.9)	0.598	15.6 (2.0)	17.7 (1.7)	0.262
Propionaldehyde		1.7 (1.7)	1.9 (1.6)	0.409	1.8 (1.7)	1.6 (1.8)	0.129	1.8 (1.7)	1.7 (1.8)	0.514	1.8 (1.8)	1.7 (1.7)	0.739
Benzaldehyde		3.6 (1.9)	3.5 (1.9)	0.934	3.7 (1.8)	3.4 (2.2)	0.527	3.5 (1.9)	3.7 (2.0)	0.661	3.9 (1.6)	3.1 (2.3)	0.060
Hexaldehyde		5.1 (1.7)	6.1 (1.7)	0.195	5.5 (1.6)	5.0 (1.8)	0.377	5.2 (1.7)	5.4 (1.6)	0.761	5.5 (1.6)	5.1 (1.8)	0.437
Benzene		3.3 (2.0)	3.4 (1.9)	0.792	3.2 (2.0)	3.3 (1.9)	0.824	3.2 (2.0)	3.5 (2.0)	0.527	2.9 (2.1)	3.8 (1.8)	0.034
n-Butanol		1.5 (1.7)	2.0 (2.0)	0.061	1.5 (1.7)	1.8 (2.0)	0.080	1.5 (1.7)	1.7 (2.0)	0.335	1.6 (1.7)	1.5 (1.9)	0.702
n-Heptane		2.8 (2.1)	3.7 (2.1)	0.090	2.6 (2.1)	3.4 (2.1)	0.053	2.7 (2.1)	3.5 (2.2)	0.063	2.6 (2.1)	3.4 (2.1)	0.045
Toluene		63.3 (2.7)	70.7 (2.8)	0.641	55.6 (2.6)	81.2 (2.8)	0.034	57.9 (2.6)	84.2 (2.9)	0.051	62.2 (2.7)	67.6 (2.7)	0.636
n-Butylacetate		2.7 (3.0)	2.9 (3.6)	0.730	2.7 (3.0)	2.8 (3.2)	0.831	2.6 (2.9)	3.0 (3.6)	0.586	2.5 (3.0)	3.0 (3.2)	0.337
n-Octane		2.2 (2.1)	3.1 (1.9)	0.072	2.2 (2.0)	2.6 (2.3)	0.321	2.2 (2.0)	2.8 (2.2)	0.083	2.2 (2.0)	2.5 (2.2)	0.431
Tetrachloroethylene	GM	0.5 (4.8)	0.9 (5.2)	0.092	0.5 (4.7)	0.5 (5.3)	0.956	0.5 (4.8)	0.5 (5.3)	0.855	0.5 (4.6)	0.6 (5.3)	0.473
Ethylbenzene	(GSD)	5.5 (2.2)	5.5 (1.7)	1.000	5.1 (2.1)	6.2 (2.0)	0.139	5.7 (2.0)	5.3 (2.4)	0.648	5.3 (2.0)	5.9 (2.2)	0.398
Xylene		10.0 (2.1)	9.8 (2.0)	0.925	9.1 (2.0)	11.4 (2.1)	0.081	9.9 (2.1)	10.1 (2.2)	0.858	9.2 (2.2)	11.0 (2.0)	0.175
Styrene		0.8 (1.9)	1.0 (1.8)	0.164	0.8 (1.9)	0.9 (1.9)	0.556	0.8 (1.9)	0.9 (2.1)	0.573	0.8 (1.9)	0.9 (2.0)	0.187
n-Nonane		1.0 (2.2)	1.2 (2.2)	0.568	1.1 (2.2)	1.0 (2.3)	0.510	1.1 (2.2)	1.1 (2.2)	0.860	1.0 (2.3)	1.1 (2.0)	0.501
1,4-dichlorobenzene		1.6 (2.8)	1.9 (1.9)	0.398	1.6 (3.0)	1.8 (2.1)	0.348	1.5 (2.9)	2.0 (1.8)	0.053	1.6 (2.8)	1.8 (2.4)	0.495
D-Limonene		2.3 (2.5)	2.4 (1.7)	0.731	2.5 (2.7)	2.1 (2.0)	0.330	2.3 (2.6)	2.3 (2.0)	0.992	2.3 (2.6)	2.4 (2.2)	0.800
Nonanal		4.4 (2.0)	4.7 (1.6)	0.554	4.4 (2.1)	4.5 (1.6)	0.775	4.4 (2.0)	4.6 (1.6)	0.593	3.9 (2.1)	5.2 (1.7)	0.013
n-Undecane		1.0 (2.2)	0.9 (1.9)	0.544	0.9 (2.2)	1.0 (2.1)	0.526	0.9 (2.3)	1.0 (2.0)	0.660	1.0 (2.4)	0.9 (1.9)	0.894
Decanal		1.2 (1.8)	1.4 (1.8)	0.334	1.2 (1.8)	1.3 (1.7)	0.473	1.2 (1.8)	1.4 (1.7)	0.194	1.1 (1.8)	1.4 (1.6)	0.023
n-Dodecane		2.5 (3.3)	3.0 (2.4)	0.558	2.2 (2.9)	3.4 (3.3)	0.027	2.3 (2.9)	3.4 (3.4)	0.072	2.4 (3.3)	2.9 (2.8)	0.276
n-Tetradecane		3.7 (2.1)	3.2 (2.2)	0.492	3.5 (2.1)	3.7 (2.0)	0.705	3.5 (2.1)	3.7 (2.1)	0.673	3.3 (2.2)	4.0 (1.9)	0.131
TVOC		292.0 (1.9)	270.1 (2.0)	0.625	278.8 (1.9)	303.7 (2.0)	0.481	279.9 (1.9)	309.8 (2.1)	0.438	286.2 (2.0)	290.9 (1.9)	0.893

Table 6. Relationships between SBS Symptom Groups and Environmental Monitoring Data.

AM, arithmetic mean; SD, standard deviation; GM, geometric mean; GSD, geometric standard deviation.

* Student's t-test

4. Discussion

Approximately 20–50% of USD store workers assessed experienced at least one SBS symptom within the last month, with the prevalence of general symptoms being the highest. Although not statistically significant, the proportion of all SBS symptoms, except for respiratory symptoms, was higher in women than in men, indicating that women are more sensitive to SBS symptoms, as has been observed in Korea previously.^[22] Other variables, such as education level, were associated with skin symptoms, which were similar to one previous study conducted upon Swedish adults at home,^[29] whereas working hours were marginally associated with general symptoms.

Most IAQ perceptions were significantly associated with one another. Correlation coefficients among unpleasant, moldy, and tobacco smoke odors were > 0.5, whereas all others were not, indicating different aspects of the IAQ. Similar findings have been reported in home environments in China, where parents reported IAQ perceptions.^[30]

Among the measured chemical substances, formaldehyde and TVOC concentrations in the USDs are regulated by the Indoor Air Quality Control Act of the Ministry of Environment in Korea, with corresponding threshold limits of 100 μ g m⁻³ and 500 μ g m⁻³, respectively. Here, formaldehyde concentrations in one store (0.8%) and TVOC concentrations in 25 stores (19.5%) exceeded these thresholds. Even then, aldehyde compounds and VOC concentrations were lower than those reported in a previous study in

Korea in 2017,^[31] where the GM of formaldehyde concentrations was 43.0 μ g m⁻³ (GSD = 2.1) and that of TVOC concentrations was 321.0 μ g m⁻³ (GSD = 2.2) across 30 USDs. Notably, the findings in the present study may have varied from those elsewhere, as the Indoor Air Quality Control Act mandates that IAQ should be measured in USD corridors, but not inside stores.

There have been no comparable studies on the relationships among individual aldehyde compounds, VOC concentrations, and subjective IAQ perception, although similar subjective IAQ indices have been used previously.^[20,30] IAQ perception was significantly associated with all SBS symptoms (except for skin symptoms) based on multivariable logistic analysis. A similar finding has been reported by Kim et al. (2019), where across 314 USD store workers in Seoul, dose-dependent relationships were observed among skin, eye irritation, respiratory, and general symptoms within the categorized IAQ perception scores.^[22]

Overall, environmental IAQ monitoring data, including the concentrations of several aldehyde compounds and VOCs, were associated with allSBS symptom groups (except for skin symptoms) according to the multivariable logistic models. Among the environmental monitoring data, most SBS symptom groups were associated with n-heptane concentrations, where the aORs of *n*-heptane were highest for eye irritation symptoms, followed by general and respiratory symptoms. Similar findings have been reported previously in Japan, where *n*-butanol, benzene, *n*-heptane, and xylene

concentrations were associated with SBS symptoms among adults who lived in newly built homes.^[10,32]

The source of *n*-heptane could be solvents and adhesives^[33] applied in the USDs, whereas shoes from shoe stores might be the sources of heptane.^[34] Furthermore, *n*-heptane can be emitted from building materials or cosmetic products.^[35] Xylene may be associated with shoes and leather goods,^[36] and benzene and xylene may be entering from outdoor automobile exhaust fumes, as most USD entrances are located in the city center near roads.^[31] Decanal might originate from ozone-initiated reactions or be associated with cooking-related activities.^[37,38] Based on data from the present study, indoor *n*-heptane, xylene, or benzene concentrations were significantly higher in fashion accessories than those in food services; whereas indoor decanal concentrations were not associated with store type (data not shown). More detailed results are under preparation for publication.

Associations of SBS symptoms with these aldehyde compounds and VOCs suggested that these chemical levels in USD stores need to be controlled to reduce SBS symptoms in workers. As controlling the products sold or cooking activities within USDs is difficult, increasing ventilation rates or using low-VOC-emission building materials may be more practical.

Formaldehyde irritates the skin, eyes, nose, and throat,^[39] and TVOC may cause similar symptoms. Formaldehyde and TVOC concentrations, as well as their relationships with SBS symptoms in indoor environments, have been previously reported,^[32,40] but some studies have not.^[18] In the present study,

indoor formaldehyde and TVOC concentrations were not associated with any SBS symptom group. This may have been because their concentrations maintained relatively low ranges in USD stores.

The association of SBS symptoms with several aldehyde compounds and VOCs indicated that indoor airborne chemicals are attributed to subjective symptoms. Here, aldehyde and VOCs were detected at a rate of > 90%, although their concentrations were relatively low. Nevertheless, there are no long-term studies on their biological effect on humans.^[32] Thepresent study suggests that SBS symptoms are associated even with such low concentrations of chemical substances, although further research is necessary to determine whether subjective SBS symptoms are associated with such low levels.

Notably, the present study could not infer that IAQ perception or environmental IAQ monitoring data were causally associated with SBS symptoms of workers, as the research was cross-sectional, and the reported SBS symptoms can vary depending on participants' sensitivity, as the objective measurements did not entail physicians' medical examinations. Because stores with environmental IAQ monitoring were selected only by workers who agreed, it may not be representative of all USD store workers in Seoul. Furthermore, the true operating characteristics of USDs may not have been reflected, as the study was conducted during the COVID-19 pandemic of 2020, and the number of customers, as well as the store working hours, may have been affected.

The IAQ monitoring was conducted during weekdays, for 30 min per USD store. Notably, this may not have fully represented in-store IAQ due to daily or hourly variability. In particular, population densities within USDs may be higher on weekends, potentially affecting IAQ. Such variations can affect the relationships between SBS symptoms and in-store IAQ of USDs. Accordingly, continuous sampling over longer time periods could more accurately measure VOC or aldehyde concentrations within stores.

The questionnaire survey and environmental monitoring were conducted as close in time as possible (the average difference in days between the questionnaire survey and IAQ monitoring was 11 ± 7 days), thereby minimizing the differences among SBS symptoms, aldehyde compounds, and VOC concentrations.

In this study, the relationship of SBS symptoms with indoor aldehyde compounds and VOC concentrations in USD stores was examined. Additionally, we examined the subjective IAQ. The subjective IAQ perception and several environmental IAQ monitoring data showed similar associations with SBS symptom groups. Therefore, subjective IAQ perception could help screen SBS symptoms related to IAQ in USDs.

5. Conclusions

Among the 128 USD stores and workers investigated here, 2–5 had experienced at least one SBS symptom within the previous month.

Categorized IAQ perceptions of workers were associated with SBS symptom groups, including eye irritation, as well as respiratory and general symptoms. Among IAQ monitoring data, the concentrations of *n*-butanol, *n*-heptane, and xylene were associated with eye irritation symptoms, while those of *n*-heptane were associated with respiratory symptoms, and those of benzene, *n*-heptane, and decanal were associated with general symptoms, showing similar trends as when IAQ perceptions were used as subjective indicators. The association of SBS symptoms with aldehyde compounds and VOCs suggests that the chemical levels in USD stores need to be controlled to reduce SBS symptoms in workers. Because managing the products sold or cooking activities within USDs is difficult, increasing ventilation rates or using low-VOC-emission building materials are likely more practical.

6. References

- [1] World Health Organization, Indoor air pollutants: exposure and health effects. Denmark: World Health Organization; 1983.
- [2] Runeson, R.; Wahlstedt, K.; Wieslander, G.; Norbäck, D. Indoor air 2006, 16, 445.
- [3] Mentese, S.; Tasdibi, D. Indoor Built. Environ. 2016, 25, 563.
- [4] Zamani, M. E.; Jalaludin, J.; Shaharom, N. Am. J. Appl. Sci. 2013, 10, 1140.
- [5] Saijo, Y.; Nakagi, Y.; Ito, T.; Sugioka, Y.; Endo, H.; Yoshida, T.

Environ. Health Prev. Med. 2010, 15, 276.

- [6] Sundell, J.; Levin, H.; Nazaroff, W. W.; Cain, W. S.; Fisk, W. J.; Grimsrud, D. T.; Gyntelberg, F.; Li, Y.; Persily, A.; Pickering, A. Indoor air 2011, 21, 191.
- [7] Bakke, J. V.; Moen, B. E.; Wieslander, G.; Norbäck, D. J. Occup.
 Environ. Med. 2007, 49, 641.
- [8] Magnavita, N. Int. Arch. Occup. Environ. Health 2015, 88, 185.
- [9] Hodgson, M. J.; Frohliger, J.; Permar, E.; Tidwell, C.; Traven, N. D.; Olenchock, S. A.; Karpf, M. J. Occup. Med. 1991, 33, 527.
- [10] Nakayama, K.; Morimoto, K. J. Hyg. 2009, 64, 689.
- [11] Lu, C.; Deng, Q.; Li, Y.; Sundell, J.; Norback, D. Sci. Total Environ.2016, 560, 186.
- [12] Wolkoff, P.; Nielsen, G. D. Atmos. Environ. 2001, 35, 4407.
- [13] Cone, J. E.; Shusterman, D. Environ. Health Perspect. 1991, 95, 53.
- [14] Nielsen, G. D. Crit. Rev. Toxicol. 1991, 21, 183.
- [15] Cain, W. S.; Cometto-Muniz, J. E. Occup. Med. 1995, 10, 133.
- [16] Kjærgaard, S. K.; Pedersen, O. F.; Taudorf, E.; Mølhave, L. Int. Arch. Occup. Environ. Health 1990, 62, 133.
- [17] Wang, J.; Li, B.; Yang, Q.; Yu, W.; Wang, H.; Norback, D.; Sundell,
 J. PLoS One 2013, 8, e72385.
- [18] Sun, Y.; Hou, J.; Cheng, R.; Sheng, Y.; Zhang, X.; Sundell, J. Energy Build. 2019, 197, 112.
- [19] Thach, T.-Q.; Mahirah, D.; Dunleavy, G.; Nazeha, N.; Zhang, Y.; Tan,

C. E. H.; Roberts, A. C.; Christopoulos, G.; Soh, C. K.; Car, J. Build. Environ. 2019, 166, 106420.

- [20] Lin, Z.; Wang, T.; Norback, D.; Kan, H.; Sundell, J.; Zhao, Z. Chin. Sci. Bull. 2014, 59, 5153.
- [21] Shang, Y.; Li, B.; Baldwin, A.; Ding, Y.; Yu, W.; Cheng, L. Build. Environ. 2016, 108, 1.
- [22] Kim, J.; Jang, M.; Choi, K.; Kim, K. BMC public health 2019, 19, 632.
- [23] Golany, G. S.; Ojima, T. Geo-space urban design, John Wiley & Sons, 1996.
- [24] Cheng, L.; Li, B.; Cheng, Q.; Baldwin, A.; Shang, Y. Build. Environ.2017, 118, 128.
- [25] Won, S. R.; Shim, I.-K.; Kim, J.; Ji, H. A.; Lee, Y.; Lee, J.; Ghim,
 Y. S. Int. J. Environ. Res. Public Health 2021, 18, 297.
- [26] Seoul Metropolitan Facilities Management Corporation, Overview of underground walkway & shopping center, https://www.sisul.or.kr/open_content/undershop/guide/summary.jsp.
- [27] Grazhdani, D. Waste Manag. 2016, 48, 3.
- [28] Kim, J.; Lee, K. Int. J. Hyg. Environ. Health 2020, 224, 113419.
- [29] Sahlberg, B.; Mi, Y.-H.; Norbäck, D. Int. Arch. Occup. Environ. Health 2009, 82, 1211.
- [30] Bu, Z.; Wang, L.; Weschler, L. B.; Li, B.; Sundell, J.; Zhang, Y. Build. Environ. 2016, 106, 167.

- [31] Won, S. R.; Ghim, Y. S.; Kim, J.; Ryu, J.; Shim, I.-K.; Lee, J. Int. J. Environ. Res. Public Health 2021, 18, 5508.
- [32] Takigawa, T.; Wang, B. L.; Saijo, Y.; Morimoto, K.; Nakayama, K.; Tanaka, M.; Shibata, E.; Yoshimura, T.; Chikara, H.; Ogino, K.; Kishi, R. Int. Arch. Occup. Environ. Health 2010, 83, 225.
- [33] Zuraimi, M.; Roulet, C.-A.; Tham, K.; Sekhar, S.; Cheong, K. D.;
 Wong, N.; Lee, K. *Build. Environ.* 2006, 41, 316.
- [34] Guo, H.; Kwok, N. H.; Cheng, H. R.; Lee, S. C.; Hung, W. T.; Li,
 Y. S. *Indoor Air* 2009, 19, 206.
- [35] Zhong, L.; Batterman, S.; Milando, C. W. Int. Arch. Occup. Environ. Health 2019, 92, 141.
- [36] Robert, L.; Guichard, R.; Klingler, J.; Cochet, V.; Mandin, C. Indoor air 2021, 31, 1238.
- [37] Ho, S. S. H.; Yu, J. Z.; Chu, K. W.; Yeung, L. L. J. Air. Waste. Manag. Assoc. 2006, 56, 1091.
- [38] S. Yang, K. Gao, X. Yang, Build. Environ. 2016, 103 146.
- [39] U.S. Environmental Protection Agency, *Facts About Formaldehyde*, https://www.epa.gov/formaldehyde/facts-about-formaldehyde#whatare.
- [40] Norbäck, D.; Hashim, J. H.; Hashim, Z.; Ali, F. Sci. Total Environ.2017, 592, 153.

Chapter 4.

Indoor Air Pollutants and Their Risk Assessments

Part II. Determinants of Indoor Particulate Matters and Gaseous Pollutants Concentrations in Different Types of Housing in Korea

1. Introduction

Although residential environments have traditionally received less attention than outdoor air or work environments, they may be the primary sources of exposure to certain air pollutants for many people. This is because people spend a significant amount of time indoors, often more than 90%.^[1,2] Additionally, efforts to improve the energy efficiency of buildings have resulted in making indoor spaces more airtight, which can increase the risk of environmental diseases such as sick house syndrome and multiple chemical sensitivity.^[3-5] Volatile organic compounds (VOCs) are a significant group of indoor air pollutants because their concentration levels are often higher indoors than outdoors.

Emissions from building materials, car exhaust, interior renovations, smoking, cooking, and poor ventilation can all contribute to poor indoor air quality.^[6-9] Previous research has shown that exposure to high levels of VOCs can have adverse health effects and contribute to the development of environmental diseases. The European exposure study (EXPOLIS) found that VOC exposure was higher at home than at outdoor or work environments. Therefore, it is important to be mindful of indoor air quality management.

The South Korean economy has experienced significant growth in recent years. Over the past decade, the country's per capita income has nearly doubled. Also, the supply of houses had already reached a point of saturation in 2002. As the economy improves, the production of building materials and chemical products used in our homes has also increased. This
means that there is a higher possibility of being exposed to more chemicals in daily activities.

The Ministry of Environment in South Korea regulates the indoor air quality of construction materials, public facilities, and newly constructed apartments in order to address indoor air quality issues.^[10] While previous research has primarily focused on the indoor air quality of newly constructed houses in the pre-occupancy stage,^[11-13] most people actually live in houses that are in the post-occupancy stage. Therefore, monitoring and evaluating indoor air quality in post-occupancy houses is considered more valuable for promoting public health. However, there is a lack of research on the systematic maintenance of indoor air quality in post-occupancy houses.

The most common types of housing in South Korea are apartments, detached houses, and multiplex houses. And the assessment of indoor air quality in these types of housing is important because approximately 47% of South Koreans live in apartments, 39% live in detached houses, and the rest live in multiplex/terraced houses.

In this study, the results of indoor air concentrations of single VOCs, TVOCs, carbonyl compounds, carbon dioxide, PM10, and PM2.5 in three most common types of housing in Korea in 2009-2010 are summarized.

This study aimed to investigate the association between housing types and indoor air quality in these dwellings and to identify factors that influence indoor air quality by summarizing the results of indoor air concentrations of

single VOCs, total VOCs, carbonyl compounds, carbon dioxide, PM10, and PM2.5 in the three most common types of housing in South Korea in 2009-2010.

2. Materials and Methods

2.1. Test Homes

Characteristics of a total of 180 dwellings were summarized in Table 1. This study involved the investigation of 100 apartments, 32 detached houses, and 48 terraced/multiplex houses in order to characterize the indoor and outdoor air quality by housing type.

The average age of the apartments, detached houses, and multiplex houses was 13.0, 22.8, and 13.8 years, respectively. The average floor of the apartments, detached houses, and multiplex houses was 7.8, 1.2, and 2.0, respectively. The mean floor of the detached houses was close to one due to the characteristics of these types of houses. The average indoor area of the apartments, detached houses, and multiplex houses was 93.6, 121.8, and 72.9 m², respectively.

	п	%
Туре		
Apartment	100	55.6
Detached	32	17.8
Terraced/multiplex	48	26.7
New furniture/renovation		
No	88	48.9
Yes	92	51.1
Year of construction		
≤ 1990	51	28.3
1991-1995	30	16.7
1996-2000	32	17.8
2001-2005	39	21.7
≥ 2006	27	15.0
Size (m^2)		
< 82.5	14	41.1
≥ 82.5	106	58.9
Floor		
Underground	6	3.3
1st-2nd	55	30.6
\geq 3rd	97	53.9

Table 1. House Characteristics.

2.2. Sampling Methods

Indoor air samples were collected during the day. Prior to sampling, the windows of all studied houses were opened for 30 minutes to ensure good ventilation, and the houses were made airtight for 5 hours. Active samplers were placed in three locations in each residence: a living room, a bedroom, and an outdoor area. In indoor locations, the sampling equipment was set up in the center of the room. The outdoor sampling position was selected to

avoid significant point sources of pollution, such as car exhaust. The height at which the sampler was set up varied depending on the nature of the home, either 1.5 m above the ground to represent the breathing zone of a standing person or 1.2 m above the ground to represent the breathing zone of a sitting person.

Temperature and relative humidity were recorded using two thermo-hygrometer data loggers (Oregon Scientific). An IAQ-CalCTM portable device (model 8760, TSI Inc., USA) was used to monitor indoor and outdoor CO_2 concentrations.

VOCs were collected using a commercial adsorbent tubes (Tenax-TA, 200 mg, $1/4" \times 9$ cm, Perkin Elmer Inc., U.K.) and a personal air sampling pump (MP- Σ 30H, Sibata scientific technology LTD, Japan) at a flow rate of 0.1 L min⁻¹ for 30 minutes. After sampling, the samples were sealed and stored at 4 °C. Field blanks were collected alongside the air samples. The VOCs collected on the adsorbent tubes were desorbed in a Thermal Desorption (TD) system (Shimadzu, Japan), separated by GC (GC-2010, Shimadzu, Japan) and detected by quadrupole mass spectrometry. The analytical column used was a VB-1 capillary column (0.25 mm internal diameter, 60 m length, 1.0 µm film thickness). The temperature program for the GC oven was as follows: 40 °C for 6 minutes, increasing at a rate of 4 °C min⁻¹ up to 180 °C, increasing at a rate of 20 °C min⁻¹ up to 250 °C, and then maintained at 250 °C for 10 minutes. The concentration of total volatile organic compounds (TVOC) was determined by analyzing the total

integrated signals between n-hexane and n-hexadecane in a GC/MS chromatogram and expressing the result as toluene equivalents.

Carbonyl compounds in the air were collected using а 2,4-dinitrophenylhydrazine (DNPH) cartridge (Supelco, USA) and a personal air sampling pump at a flow rate of 0.5 L min-1 for 30 minutes. An ozone scrubber (Sep-Pak, Waters, USA) was installed in front of the DNPH cartridge to eliminate the influence of ozone. The amounts of three target carbonyl compounds (formaldehyde, acetaldehyde, and acetone) were then analyzed using high performance liquid chromatography (HPLC). The indoor and outdoor PM10 and PM2.5 concentrations were monitored using a SidePak Aerosol Monitor (model AM510, TSI Inc., USA), which measured PM10 and PM2.5 at 5-second intervals at a flow rate of 1.7 L min⁻¹ for 10 minutes.

2.3. Data Analysis

Data analysis for this study was conducted using SPSS 12.0 to calculate descriptive statistics, perform multiple regression analysis, and use non-parametric methods such as One Way ANOVA. The Pearson correlation coefficient was used to determine correlations between quantitative indoor air quality variables (pollutant concentrations, temperature, relative humidity, floor, housing type, season, construction years, etc.). Statistically significant associations were identified as those with a p-value of less than 5% for a two-sided test.

3. Results and Discussion

3.1. Indoor pollutants concentration of three different housing types

Table 2 shows the concentrations of various indoor pollutants in different types of housing. The most common chemicals found were toluene, ethylbenzene, xylene, styrene, formaldehyde, acetaldehyde, and acetone. The concentrations of all single volatile organic compounds (VOCs) except for toluene were higher in multiplex houses compared to apartments. The concentration of total VOCs (TVOCs) generally ranged from 50 to 5,500 µg m^{-3} in the studied houses, with mean concentrations of 651.5 µg m^{-3} in apartments, 701.4 μ g m⁻³ in detached houses, and 808.5 μ g m⁻³ in multiplex houses. The highest TVOC concentration, around 5,417.9 μ g m⁻³, was recorded in one of the apartments studied. This apartment had indoor dimensions of 32.0 m³, similar to the average dimensions of 33.1 m³ for the other apartments. The total volume of furniture in this apartment was 6.84 m^3 , similar to the average dimensions of all furniture in each apartment. The indoor temperature of this apartment (26.0 °C) was also not significantly different from the average indoor temperature of the other apartment houses (26.4 °C). Therefore, it is assumed that some anthropogenic sources of TVOC (e.g., adhesive, raw wood, wood based panel,^[14] air freshener) rather than environmental factors (temperature, dimension of indoor space) had a significant effect on the concentration.

									(ur	nit: ug n	n ⁻³ except	for CO_2)
	Apartment (n=400)				Detached houses (n=150)			Multiplex houses (n=226)				
	Mean	Min	Median	Max	Mean	Min	Median	Max	Mean	Min	Median	Max
Toluene	114.7	12.2	75.9	831.3	110.7	4.1	38.8	1,796.7	92.3	3.7	60.8	820.8
Ethylbenzene	10.4	N.D.	7.0	98.9	10.5	N.D.	4.9	111.8	24.3	N.D.	7.0	465.4
Xylene	19.0	N.D.	14.6	99.9	16.8	N.D.	9.8	155.9	46.1	N.D.	12.8	1,692.7
Styrene	9.8	N.D.	4.4	119.5	5.4	N.D.	1.6	94.2	15.9	N.D.	3.2	897.3
TVOC	651.5	78.9	507.1	5,417.9	701.4	55.9	439.7	4,056.3	808.5	50.7	591.6	4,355.2
Formaldehyde	130.0	24.2	119.2	350.6	99.5	8.7	75.1	414.6	127.0	11.1	102.5	511.8
Acetaldehyde	37.6	N.D.	33.7	120.0	31.4	0.9	27.1	169.6	44.4	6.4	37.6	186.2
Acetone	80.7	14.2	65.4	566.3	66.2	13.7	56.0	327.3	98.3	12.0	82.2	390.6
CO ₂ (ppm)	961	366	846	2,784	1,019	311	963	2,321	1,377	387	1,272	4,606
PM _{2.5}	48.4	4.0	40.0	266.0	57.6	3.0	53.0	241.0	51.4	8.0	42.0	306.0
PM ₁₀	53.8	6.0	44.5	284.0	61.8	4.0	58.0	249.0	55.6	8.0	45.0	306.0

Table 2. Comparison of Indoor Air Pollutant Concentrations in Different Housing Types.

* N.D.: not detected.

The high concentration of total volatile organic compounds (TVOC) in the indoor air of this apartment house was likely due to the high levels of d-limonene, n-hexane, nonanal, and n-undecane. These VOCs were found to be 6.5, 7.6, 10.4, and 14.9 times higher than the average concentration in the other monitored apartment houses, respectively. D-limonene is a chemical commonly found in indoor air and is associated with citrus fruit and air fresheners.^[15,16] Limonene is generally considered safe, but sometimes it may cause irritation to the eyes, skin, and throat in humans, and has been shown to cause kidney damage in rats.^[17] Nonanal is emitted by paper and perfumes, and n-undecane can be found in indoor air as a result of cigarette smoking and painting.^[18] It is likely that indoor smoking and the presence of tangerines, and wet painting on the walls in the house contributed to the high TVOC concentration.

The average and maximum concentrations of styrene in multiplex houses were significantly higher than in other types of housing. This may be due to the fact that many multiplex houses have vinyl flooring sheets,^[19] which contain styrene, rather than wood-based tiles, which are commonly used in apartments and detached houses. The high levels of styrene emitted from the vinyl flooring sheets likely have a significant impact on the indoor air quality in multiplex housing.

The maximum CO_2 concentration was recorded in a multiplex housing, as shown in Table 2. The highest CO_2 concentration is probably due to the relatively small indoor volume of this detached house (20.00 m³). The

average indoor dimensions of apartments, detached houses, and multiplex houses are 33.07, 44.47, and 29.40 m³, respectively.

Formaldehyde levels in detached houses were slightly lower compared to other housing types. The average concentration of formaldehyde in apartments, detached houses, and multiplex houses was 130.0, 99.5, and 127.0 μ g m⁻³, respectively. These values in apartments and multiplex houses exceed the Ministry of Environment's guidelines (210 μ g m-3) for newly constructed apartments.

However, no notable differences were found among the housing types in terms of particulate matter.

3.2. Indoor/outdoor ratio

Table 3 presents the ratio of indoor to outdoor concentrations (I/O ratio) of major indoor chemicals. The sample sizes for each of the measured pollutants in apartments, detached houses, and multiplex houses are 400, 150, and 226, respectively. Except for particulate matter, all indoor-to-outdoor ratios were above one. This indicates that indoor sources have an impact on the indoor air quality in the studied houses.^[20,21]

When comparing the mean values of the I/O ratio, multiplex houses had higher indoor levels of total gaseous pollutants than apartments and detached houses. In particular, the I/O ratio of styrene, which is possibly a human carcinogen, was above 70 in apartments. This significant difference may be due to the extensive use of plastic home appliances within a confined indoor space. The low outdoor concentration of styrene in apartment complexes also contributes to a higher I/O ratio compared to the other housing types. The average outdoor concentrations of styrene are 0.14 μ g m⁻³ in apartment complexes, 0.30 μ g m⁻³ in detached houses, and 3.0 μ g m⁻³ in multiplex houses, respectively. The reason of this outdoor level difference could be explained by the fact that potential styrene-emitting recyclable materials such as plastic products are well-managed by being collected in designated areas in apartments, while recyclables are often stacked close to the buildings in multiplex houses.

In the case of particulate matter, concentrations are higher outdoors than indoors due to vehicle emissions and other factors.

	Apartments (n=400)	Detached houses $(n=150)$	Multiplex houses $(n=226)$
Toluene	4.1	4.9	4.1
Ethylbenzene	2.2	2.8	6.4
Xylene	3.4	3.4	9.5
Styrene	70.7	2.7	8.1
TVOC	9.5	11.1	12.8
Formaldehyde	9.0	6.6	8.5
Acetaldehyde	8.1	7.8	11.0
Acetone	9.6	3.8	5.6
CO_2	3.9	3.0	4.1
PM _{2.5}	0.8	0.7	0.7
PM ₁₀	0.8	0.7	0.7

 Table 3. Indoor to Outdoor Ratios of the Concentration of Indoor Air

 Pollutants in Apartment, Detached houses and Multiplex Houses.

3.3. Affection factors on indoor air quality

3.3.1. Interior renovation

Residential houses in Melbourne, Australia that have undergone renovations have been reported to have indoor concentrations of volatile organic compounds that are 10 to 100 times higher, and this high level persists for several months.^[15] And this high concentration of volatile organic compounds decreases significantly within the following year and after one year, the variation becomes very small.^[22]

To investigate the effect of interior renovations on indoor air quality, an additional survey was conducted on the studied houses, and the results are summarized in Table 4. The data was analyzed using the Mann-Whitney test to determine the significance of four sets of data groups. As a result, most chemical measurements generally recorded higher values in homes whose period after the completion of interior renovations was within a year, compared to those that were over a year. In particular, the concentration of toluene was almost twice as high and formaldehyde was almost 50% higher in interior remodeled apartments and detached houses. This indicates that certain indoor sources significantly contribute to indoor air quality. Although formaldehyde is known to be emitted by numerous natural sources and anthropogenic activities, it is extensively produced by man-made products, particularly indoors. Formaldehyde and toluene are widely used as solvents or additives in the production of off-gassing products such as new wooden

products, recent paint or varnish, ceiling tiles, carpet glues, various plastics, and insulation materials.^[23-25]

Therefore, the latter outweighed the former as a major indirect source of formaldehyde and toluene in recently renovated spaces. Although acetone is widely used as a solvent in many interior materials,^[26] the Wilcoxon rank sum tests of significance showed no statistically significant difference between non-renovated houses and renovated houses within one year. TVOC levels also exhibited significant differences regardless of housing type, but the difference in average concentration between them was only statistically significant in detached houses (P<0.05).

In the case of particulate matter, PM2.5 and PM10 levels were slightly lower in renovated houses, but it was not statistically significant.

	Apartment		Detached hous	ses	Multiplex hou	Multiplex houses		
	Yes (n=80)	No (<i>n</i> =320)	Yes (n=30)	No (<i>n</i> =120)	Yes (<i>n</i> =60)	No (<i>n</i> =164)		
Toluene	205.9**	91.9**	181.4**	93.0**	93.2	91.9		
Ethylbenzene	14.2**	9.4**	14.5**	9.5**	54.2*	13.0*		
Xylene	23.6*	17.9*	22.7**	15.3**	116.1**	19.7**		
Styrene	15.8**	7.0**	5.1	5.5	38.3	7.4		
TVOC	752.2**	626.4**	881.2**	656.4**	915.5	768.0		
Formaldehyde	168.4**	120.4**	135.2*	90.6*	124.3	128.0		
Acetaldehyde	43.1*	36.2*	35.6	30.4	41.1	45.6		
Acetone	111.8**	72.9**	77.4	63.2	101.3	96.9		
PM _{2.5}	38.6	50.7	56.7	57.8	48.0	52.8		
PM ₁₀	43.3	56.2	61.0	61.9	51.7	57.1		

Table 4. Association between Indoor Pollutants Levels and Interior Renovations.

* Mann-Whitney *p<0.05, **p<0.01

3.3.2. Length of residence

Each housing type is divided into two groups to examine how the length of residence affects indoor air quality in residential spaces. As shown in Table 5, one group consists of current occupants who have lived there for less than two years, and the other group has lived there for over 11 years. All chemical levels detected in studied houses dramatically decreased with occupancy time, except for TVOC levels in apartments. For residences with less than five years of occupancy, the concentration of BTEX is statistically significant, and it is thought that the shorter the dwelling period means that the house will be a newly built building with a high probability.^[27]

Additionally, newly built houses have higher indoor pollutant levels because the air is more tightly contained compared to older, more ventilated houses.^[22,28] In particular, the average concentrations of styrene significantly decreased over time, which may be due to the lack of new off-gassing sources or plastic-based home electronics such as TVs, refrigerators, microwaves, and computers.

	Apartment		Detached houses		Multiplex houses		
	\leq 2years (<i>n</i> =168)	\geq 11years (n =32)	\leq 2years (n = 38)	\geq 11 years (n = 72)	\leq 2years (n =86)	\geq 11 years (n =12)	
Toluene	161.9**	76.5**	276.5**	44.3**	117.2*	44.6*	
Ethylbenzene	12.7	7.9	14.7 [*]	6.6*	41.7**	3.2**	
Xylene	22.5	13.8	24.0*	12.5*	88.8**	8.9**	
Styrene	13.1**	3.3**	15.1**	2.3**	32.8**	1.1**	
TVOC	712.9	725.2	1,029.5**	538.0**	924.6*	452.0 [*]	
Formaldehyde	143.0**	87.1**	172.2**	79.1**	145.3	104.7	
Acetaldehyde	37.9	31.9	44.3**	25.5**	46.9	37.2	
Acetone	92.6**	48.6**	83.5**	55.8**	113.2*	62.8*	
PM _{2.5}	42.9	45.3	58.7	56.6	45.1	38.1	
PM_{10}	47.8	49.9	61.7	61.4	48.8	40.7	

Table 5. Association between Indoor Pollutants Levels and Length of Residence.

* Mann-Whitney *p<0.05, **p<0.01

3.3.3. Floor

To study the relationship between indoor pollutant levels and floor, the studied houses were classified into two or three sub-groups based on their floor and the results are summarized in Table 6.

The concentrations of carbonyl compounds in apartments were significantly associated with the floor (P<0.05) and increased with higher floor levels. In the case of detached/multiplex houses, only TVOC and formaldehyde concentrations showed a statistical difference with the floor.

In contrast, individual VOCs and particulate matter levels did not show a significant association with the floor.

	Apartment		Detached/Multiplex houses			
	1 st ~2 nd (<i>n</i> =136)	$\geq 3^{\rm rd}$ (<i>n</i> =264)	Underground (n=24)	1 st ~2 nd (<i>n</i> =112)	$\geq 3^{\rm rd}$ (<i>n</i> =90)	
Toluene	114.5	114.8	92.5	79.5	108.1	
Ethylbenzene	10.5	10.4	9.7	35.4	14.2	
Xylene	20.6	18.3	22.0	66.5	27.2	
Styrene	7.6	10.9	4.1	7.7	29.2	
TVOC	650.4	652.1	1,334.1**	692.4**	812.7**	
Formaldehyde	110.8**	139.8**	85.9 [*]	128.8*	135.7*	
Acetaldehyde	35.0**	38.9**	41.7	43.9	45.6	
Acetone	65.6**	88.0^{**}	105.0	95.2	100.6	
PM _{2.5}	52.4	45.9	51.1	50.4	52.9	
PM_{10}	58.2	51.0	56.6	53.9	57.5	

Table 6. Association between Indoor Pollutants Levels and Floor.

* (Apartment) Mann-Whitney *p<0.05, **p<0.01, (Detached/Multiplex houses) Kruskal-Wallis * p<0.05, ** p<0.01

3.3.4. Season

Figure 1 illustrates the average values of residential indoor pollutants according to the four seasons: spring (March to May), summer (June to August), fall (September to November), and winter (December to February).

The indoor temperature and humidity during the spring season was 22.2 °C and 48.7%, respectively. During the summer season, the indoor temperature and humidity was 28.3 °C and 64.1%, respectively. During the fall season, the indoor temperature and humidity was 22.7 °C and 54.6%, respectively. During the winter season, the indoor temperature and humidity was 19.2 °C and 45.6%, respectively.

There are several reports about variations of residential indoor pollutants levels by seasons. Some reports suggest that the higher levels of residential indoor pollutants during the winter season may be due to the colder, harsher weather conditions, which may result in closed windows and decreased ventilation. For example, in Britain, it has been reported that there are higher concentrations of VOCs (208 μ g m⁻³) in residential homes during the winter season compared to the summer season (161 μ g m⁻³).^[30] In Germany, there are also reports of higher concentrations of major VOCs, including benzene, during the winter season compared to other seasons.^[31] However, there are also reports that suggest the opposite trend. For instance, in German apartments, VOC concentrations have been reported to be approximately four times higher during the summer season.^[32] This observation has been interpreted as being the result of the increase in indoor

temperature from the hot summer weather, which may facilitate the release of VOCs from furnishings. Both relative indoor humidity and temperature have been found to be closely related to indoor VOC emissions.^[33]

In our research, we observed elevated concentrations of VOCs, including toluene and aldehydes, in summer due to the fact that the indoor summer temperature was approximately 9 °C higher on average than the winter conditions.



Figure 1. Seasonal variation of indoor air pollutants in studied houses.

4. Conclusions

In this study, a detailed investigation of indoor air quality was conducted in the three most common types of housing. The average concentrations of chemicals found in the studied houses were higher than those previously reported for houses in countries with a similar climate. The levels of styrene were significantly higher in apartments compared to the other housing types. Formaldehyde concentrations in apartments and detached houses were found to be influenced by the interior building materials. Other factors, such as length of residence and floor location, also had an impact on indoor air quality, although the magnitude of this impact varied among the different housing types and characteristics.

5. References

- [1] Jia, C.; Batterman, S.; Godwin, C., Atmos. Environ. 2008, 42, 2083.
- [2] Klepeis, N. E.; Nelson, W. C.; Ott, W. R.; Robinson, J. P.; Tsang, A. M.; Switzer, P.; Behar, J. V.; Hern, S. C.; Engelmann, W. H. J. Expo. Anal. Environ. Epidemiol. 2001, 11, 231.
- [3] Molhave, L. Indoor Air 2003, 13, 12.
- [4] Wolkoff, P.; Nielsen, G. D. Atmos. Environ. 2001, 35, 4407.
- [5] Wieslander, G.; Norrbäck, D.; Björnsson, E.; Janson, C.; Boman, G. Int. Arch. Occup. Environ. Health 1997, 69, 115.
- [6] Hun, D. E.; Corsi, R. L.; Morandi, M. T.; Siegel, J. A. Build. Environ.

2011, 46, 45.

- [7] Abdullahi, K. L.; Delgado-Saborit, J. M.; Harrison, R. M. Atmos. Environ. 2013, 71, 260.
- [8] Konstantopoulou, S. S.; Behrakis, P. K.; Lazaris, A. C.;
 Nicolopoulou-Stamati, P. Sci. Total Environ. 2014, 476, 136.
- [9] Uhdea, E.; Salthammer, T. Atmos. Environ. 2007, 41, 3111.
- [10] Ministry of Environment. Indoor Air Quality Management Act., Republic of Korea, 2003.
- [11] Baek, S. -O.; Kim, Y. -S.; Perry, R. Atmos. Environ. 1997, 31, 529.
- [12] Sohn, J. -Y.; Jo, W. -J. Build. Environ. 2009, 44, 1794.
- [13] Jo, W. -K.; Lee, J. -Y. Atmos. Environ. 2006, 40, 6067.
- [14] Jiang, C.; Li, S.; Zhang, P.; Wang, J. Build. Environ. 2013, 69, 227.
- [15] Brown, S. K.; Sim, M. R.; Abramson, M. J.; Gray, C. N. Indoor Air 1994, 4, 123.
- [16] Nazaroff, W. W.; Weshcler, C. J. Atmos. Environ. 2004, 38, 2841.
- [17] International Agency for Research on Cancer. Some chemicals that cause tumours of the kidney or urinary bladder in rodents and some other substances: IARC monographs on the evaluation of carcinogenic risks to humans; World Health Organization, 1999.
- [18] Edwards, R. D.; Jurvelin, J.; Saarela, K.; Jantunen, M. Atmos. Environ.2001, 35, 4531.
- [19] Järnström, H.; Saarela, K.; Kalliokoski, P.; Pasanen, A. -L. Atmos. Environ. 2006, 40, 7178.

- [20] Lee, S. C.; Li, W. M.; Ao, C. H. Atmos. Environ. 2002, 36, 225.
- [21] USEPA. Indoor air quality: sick building syndrome (EPA/402-F-94-004);Indoor Air Group, Research Triangle Park, North Carolina, 1991.
- [22] Park, J. S.; Ikeda, K. Indoor Air 2006, 16, 129.
- [23] Kelly, T. J.; Smith, D. L.; Satola, J. Environ. Sci. Technol. 1999, 33, 81.
- [24] Morrison, G. C.; Nazaroff, W. W. Atmos. Environ. 2002, 36, 1749.
- [25] Morrison, G. C.; Nazaroff, W. W. Environ. Sci. Technol. 2002, 36, 2185.
- [26] Liu, W.; Zhang, J.; Zhang, L.; Turpin, B. J.; Weisel, C. P.; Morandi, M. T.; Stock, T. H.; Colome, S.; Korn, L. R. Atmos. Environ. 2006, 40, 2202.
- [27] D'Souza, J. C.; Jia, C.; Mukherjee, B.; Batterman, S. Atmos. Environ.2009, 43, 2884.
- [28] Jones, A. P. Atmos. Environ. 1999, 33, 4535.
- [29] Rehwagen, M.; Schlink, U.; Herbarth, O. Indoor air 2003, 13, 283.
- [30] Raw, G. J.; Coward, S. K. D.; Brown, V. M.; Crump, D. R. J. Expo. Anal. Environ. Epidemiol. 2004, 14, 85.
- [31] Ilgen, E.; Karfich, N.; Levsen, K.; Angerer, J.; Schneider, P.; Heinrich, J.; Wichmann, H.-E.; Dunemann, L.; Gegerow, J. Atmos. Environ. 2001, 35, 1235.
- [32] Schlink, U.; Rehwagen, M.; Damm, M.; Richter, M.; Borte, M.; Herbarth, O. Atmos. Environ. 2004, 38, 1181.
- [33] Jarnstrom, H.; Saarela, K.; Kalliokoski, P.; Pasanen, A. Atmos. Environ.2006, 40, 7178.

Appendix

Fabrication of Wrinkled Silica Nanoparticles for VOCs abatement in air

1. Introduction

As described in Chapter 2, wrinkled mesoporous silica could be developed as various adsorbents with high performance. The character of WSNs (e.g., large specific surface area, high porosity, ease of surface modification, synthesis in mild condition, simple synthesis method, and high possibility of mass production) open up the possibility of developing WSNs to be commercial adsorbents. Although the BTEX are the most frequently detected in indoor air, numerous other volatile organic compounds are co-existed and induce sick house syndrome and multiple chemical sensitivity to humans. However, the kind of these unknown VOCs are diversifying due to the increased air tightness of buildings for energy savings and unintentional use of chemical products. From the informative annex of ISO 16000 part 5 and part 6,^[1,2] there are 44 organic chemicals listed in Table 1 that are mainly detected in indoor air. For that reason, World Health Organization (WHO) announced in 2022 that household air pollution was responsible for an estimated 3.2 million deaths per year in 2020, including 237,000 deaths of children under the age of 5.^[3]

In this appendix, the total adsorption capacities of WSNs for 44 chemicals in air were investigated.

No.	Compounds	Molecular formula		Molecular weight	Boiling point (°C)	Density
1	Hexane	CH ₃ (CH ₂) ₄ CH ₃	110-54-3	86.18	69	0.659
2	Chloroform	CHCl ₃	67-66-3	119.38	61	1.492
3	1,2-Dichloroethane	ClCH ₂ CH ₂ Cl	107-06-2	98.96	83	1.256
4	2,4-Dimethylpentane	(CH ₃) ₂ CHCH ₂ CH(CH ₃) ₂	108-08-7	100.2	80	0.673
5	1,1,1-Trichloroethane	CH ₃ CCl ₃	71-55-6	133.4	74~76	1.336
6	n-Butanol	C ₄ H ₁₀ O	71-36-3	84.16	64	0.673
7	Benzene	C ₆ H ₆	71-43-2	78.11	80	0.879
8	Carbon tetrachloride	CCl ₄	56-23-5	153.82	76	1.594
9	1,2-Dichloropropane	CH ₃ CH(Cl)CH ₂ Cl	78-87-5	112.99	95~96	1.155
10	Bromodichloromethane	CHBrCl ₂	75-27-4	163.83	90	1.98
11	Trichloroethylene	ClCH=CCl ₂	79-01-6	131.39	86.7	1.463
12	Isooctane	(CH ₃) ₂ CHCH ₂ C(CH ₃) ₃	540-84-1	114.23	98~99	0.692
13	<i>n</i> -Heptane	CH ₃ (CH ₂) ₅ CH ₃	142-82-5	100.21	98	0.684
14	Methyl Isobutyl Ketone	(CH ₃) ₂ CHCH ₂ COCH ₃	108-10-1	100.16	117	0.7978
15	Toluene	C ₆ H ₅ CH ₃	108-88-3	92.14	110.6	0.866
16	Dibromochloromethane	ClCHBr ₂	124-48-1	208.28	119~120	2.451
17	Butyl acetate	CH ₃ COO(CH ₂) ₃ CH ₃	123-86-4	116.2	124~126	0.882
18	<i>n</i> -Octane	CH ₃ (CH ₂) ₆ CH ₃	111-65-9	114.23	118	0.705
19	Tetrachloroethylene	Cl ₂ C=CCl ₂	127-18-4	165.83	121	1.622
20	Ethylbenzene	C ₆ H ₅ Cl	100-41-4	106.17	136	0.867
21	<i>m</i> -Xylene <i>p</i> -Xylene	C ₆ H ₄ (CH ₃) ₂	108-38-3 106-42-3	106.17	138	0.864
22	o-Xylene	$C_6H_4(CH_3)_2$	95-47-6	106.17	138	0.864
23	Styrene	C ₆ H ₅ CH=CH ₂	100-42-5	104.15	145~146	0.909
24	<i>n</i> -Nonane	CH ₃ (CH ₂) ₇ CH ₃	111-84-3	128.26	151	0.72
25	a-Pinene	$C_{10}H_{16}$	80-56-8	136.26	156	0.9
26	<i>m</i> -Ethyltoluene	$C_2H_5C_6H_4CH_3$	620-14-4	120.19	158~159	0.865
27	p-Ethyltoluene	$C_2H_5C_6H_4CH_3$	622-96-8	120.19	162	0.861
28	1,2,3-Trimethylbenzene	$C_{6}H_{3}(CH_{3})_{3}$	526-73-8	120.19	175~176	0.894
29	o-Ethyltoluene	$C_2H_5C_6H_4CH_3$	611-14-3	120.19	164~165	0.887
30	β-Pinene	$C_{10}H_{16}$	127-91-3	136.24	158~166	0.864
31	1,2,4-Trimethylbenzene	$C_{6}H_{3}(CH_{3})_{3}$	95-63-6	120.19	168	0.876
32	n-Decane	CH ₃ (CH ₂) ₈ CH ₃	124-18-5	142.28	174	0.73
33	1,4-Dichlorobenzene	$C_6H_4Cl_2$	106-46-7	147	173	1.241
34	1,3,5-Trimethylbenzene	$C_{6}H_{3}(CH_{3})_{3}$	108-67-8	120.19	162~164	0.865
35	D-Limonene	CH ₃ C ₆ H ₈ C(CH ₂)CH ₃	5989-27-5	136.24	178	0.8411
36	Nonanal	C ₉ H ₁₈ O	124-19-6	142.27	190	0.8264
37	n-Undecane	CH ₃ (CH ₂) ₉ CH ₃	1120-21-4	156.31	196	0.74
38	1,2,4,5-Tetramethylbenzene	$(CH_3)_4C_6H_2$	95-93-2	134.22	191~197	0.838
39	Decanal	CH ₃ (CH ₂) ₈ CHO	112-31-2	156.3	207~209	0.8
40	n-Dodecane	CH ₃ (CH ₂) ₁₀ CH ₃	112-40-3	170.34	216.2	0.749
41	n-Tridecane	CH ₃ (CH ₂) ₁₁ CH ₃	629-50-5	184.37	235	0.7564
42	<i>n</i> -Tetradecane	CH ₃ (CH ₂) ₁₂ CH ₃	629-59-4	198.4	254	0.767
43	n-Pentadecane	CH ₃ (CH ₂) ₁₃ CH ₃	629-62-9	212.42	271	0.7685
44	n-Hexadecane	$CH_3(CH_2)_{14}CH_3$	544-76-3	226.45	287	0.773

Table 1. Frequently Detected VOCs in Indoor Air and Their Properties.

2. Experimental

2.1. Chemicals and instrumentation

(3-trimethoxysilylpropyl)diethylenetriamine (DETAS) and 44 component indoor air standard (100 μ g mL⁻¹) were purchased from TCI and Supelco, respectively. All the other chemicals and instrumentation details were identical described in Chapter 2.

2.2. Surface modification of WSN

The surfactant extracted WSNs (WSN) were prepared by going through identical procedures stated in Chapter 2. To give a definite surface functionality, surface modifications were processed by a two step reaction (Appendix/Figure 1.(b)). First, hydroxyl groups on WSN were exchanged with an equal number of amine groups by condensation reaction with DETAS. 0.5 g of WSN were put into 100 mL of ethanol and strongly stirred to disperse them well. Subsequently, 242.75 μ L of DETAS corresponding to 50 wt% of WSN was added and reacted at room temperature for 24 h. Thereafter, the solution was centrifuged to precipitate the nanoparticles, washed three times using ethanol, and then dried to prepare silica nanoparticles having a wrinkled surface modified with an amine group (WSN-DETAS).

The WSN-DETAS was used as a starting material for further surface modifications. Three different coupling agents, 1,2-epoxyoctadecane (OCT),

1,3-bis(3-chloropropyl)tetrakis(trimethylsiloxy)disiloxane (DIS), 9-chloromethyl anthracene (ANT), were employed with WSN-DETAS to prepare WSN-ANT, WSN-DIS, and WSN-OCT as described in Appendix/Scheme 1.(b).



Appendix/Figure 1. (a) Coupling agents for surface modification, (b) Schematic procedure for preparing surface modified WSNs.

2.3. VOCs adsorption performance of four different WSNs

Four sorbent samples were prepared by individually packing 100 mg of WSN, WSN-ANT, WSN-DIS, and WSN-OCT with quartz wool in thermal desorption glass tubes (1/4" OD \times 3.5" length; Supelco), which were subsequently sealed as shown in Appendix/Figure 2.

For adsorption experiments, standard solutions of 44 volatile organic compounds were prepared at 500 ppm. The volatile organic compound standard used was a liquid standard mixture (100 ppm, Japanese indoor air standards mixture, Supelco). Adsorption capacities of WSNs were compared with the commercial adsorbent Tenax-TA (200 mg). The other experimental details were identical as described in Chapter 2 (Part I).



Appendix/Figure 2. (a) WSNs packed thermal desorption glass tubes, (b) diagram of common thermal desorption tube.

3. Results and Discussion

3.1. Sample characterization

The TGA curves of the WSNs were shown in Appendix/Figure 3(a). The surface-modified WSNs (WSN-DETAS, WSN-ANT, WSN-DIS, and WSN-OCT) exhibited a rapid weight loss in a temperature range from 240 to 550 °C. The weight loss ratios of the WSN, WSN-DETAS, WSN-ANT,

WSN-DIS, and WSN-OCT were about 8%, 16%, 21%, 16.5%, and 16.5%, respectively.



Appendix/Figure 3. (a) Thermogravimetric analysis curves and (b) FT-IR spectra of WSNs, (c) fluorescence spectrum of WSN-ANT.

Appendix/Figure 3(b) showed the FT-IR spectra of WSNs and fluorescence emission spectrum of WSN-ANT. In FT-IR spectra, the peaks in a range of 2850-2900 cm⁻¹ in were assigned to the symmetric and asymmetric stretching modes of the C_{sp3}-H and C_{sp2}-H. And in lower wavelength region, the peaks about at 1500 cm⁻¹ were detected due to CH₂

scissoring and CH_3 bending. Anthracene grafted WSN showed the intensity of fluorescence emitted by anthracene molecules as a function of the wavelength of the light (Appendix/Figure 3(c)). Anthracene is a polycyclic aromatic hydrocarbon (PAH) that exhibits fluorescence when excited by ultraviolet light. The characteristic peaks of anthracene means that anthracene molecules attach tightly on the surface of WSN.

3.2. VOCs Adsorption capacities of WSNs

Appendix/Figure 4 showed the test results for 44 VOCs adsorption capacities with WSN, WSN-ANT, WSN-DIS, and WSN-OCT at room temperature.

As a result of adsorption of aliphatic hydrocarbons, all WSN samples showed adsorption for higher ability except n-hexane and 2,4-dimethylpentane 2,6-diphenyl-p-phenylene than the oxide based commercial adsorbent. Among the WSNs, surface modified ones recorded higher performance than WSN. In addition, the adsorption result of aromatic hydrocarbons showed a relatively better adsorption degree than that of aliphatic hydrocarbons.

In Appendix/Figure 4(c), all aldehyde compounds showed very low interaction forces with all WSNs than Tenax-TA.



Appendix/Figure 4. Adsorption capacities of WSNs for (a) aliphatic hydrocarbons, (b) aromatic hydrocarbons, (c) aldehyde, alcohol, and acetate, (d) ketone and terpene.

4. Conclusions

The surface of wrinkled mesoporous silica were successfully modified with three different coupling agents (9-chloromethyl anthracene, 1,2-epoxyoctadecane, 1,3-bis(3-chloropropyl)tetrakis(trimethylsiloxy)disiloxane). Surface modified WSNs showed much higher adsorption performance for 44 volatile organic compounds in air rather than commercial sorbents (Tenax-TA) except for aldehydes, n-hexane, and 2,4-dimethylpentane. It is thought that further research is needed for a detailed interpretation of these results.

5. References

- [1] ISO 16000-5:2007. https://www.iso.org/standard/37388.html (accessed November 27, 2022).
- [2] ISO 16000-6:2021. https://www.iso.org/standard/73522.html (accessed November 27, 2022).
- [3] WHO, Household air pollution and health. 2022.

Abstract in Korean

나노물질은 거대 비표면적, 다양한 표면 개질 가능성 등 그 고유의 특성으로 인하여 전자, 에너지, 의학, 환경, 재료 분야에 활용되고 있다. 코로나-19 이후 사람들의 관심이 실내공기질로 집중되면서 나노물질을 실내공기 오염물질 저감에 활용하는 방안에 대한 요구가 크게 증가있다. 지금까지 수질 또는 공기 중 오염물질을 흡착하는 재료로는 활성탄, 탄소 나노튜브, 수산화 이중층, 그라핀, 다공성 실리카 등 다수의 나노물질들이 제안되고 있다.

본 학위논문은 다공성 실리카와 산화 그라핀 나노물질을 응용하여 실내공기 중의 유해 화학물질을 제거하는 효율적 흡착제 개발을 주로 다룬다. 수질 등 다른 매질과는 달리 공기 중의 오염물질 저감 평가 방법은 공기의 매질 고유특성으로 인하여 결과 값의 변이 계수가 커질 가능성이 높다. 이를 고려하여 본 학위논문에서 사용된 평가 방법론은 시편 제작 방법부터 정량적 분석방법까지 실험 전반에 걸쳐 국제표준 (ISO)을 준용하였다.

제1장에서는 본 학위논문 연구의 기초 배경에 대해 실내공기 오염물질, 흡착제, 메조다공성 실리카, 산화 그라핀에 대해 간략하게 기술하였다.

제2장에서는 표면이 주름진 메조다공성 실리카를 이용하여 표면 개질이 실내공기 중 벤젠, 톨루엔, 에틸벤젠, 자일렌 흡착에 어떤 영향을 주는지 물리적 흡착 관점에서 살펴보았다. 제안된 실리카는 벤젠을 제외한 오염 물질에 대하여 90% 이상의 제거 성능을 보여주었다.
낱개의 산화 그라핀 층은 고유의 특성으로 인하여 재조합하는 경향을
가진다. 이를 물리적으로 방지하고자 3차원 구조를 가지는 산화 그라핀
구조체를 만들고 이중 일부는 표면에 질소 원소를 도핑한 형태로 합성
하였다. 3차원 구조를 가지는 메조다공성 산화그라핀 나노입자의 실내공기
중 폼알데하이드의 저감 성능을 화학적 흡착 관점에서 주고 고찰하였으며,
상대습도 정도에 따라 그 편차가 있었으나 85.8~44.3%의 제거 성능을
확인할 수 있었다.

제3장에서는 우리나라 실내공기 오염물질의 실태조사와 그 결과를 활용한 위해성 평가를 수행한 내용을 담았다. 지하도상가 근로자가 겪는 새집증후군과 실내공기 오염물질 농도와의 상관관계를 살펴보았다. 부탄올, 헵탄, 자일렌의 농도는 눈 점막 자극 증상과 관련이 있었고, 호흡기 증상은 헵탄, 일반적인 새집증후군 증상은 벤젠, 헵탄, 데칸알의 농도와 관계가 있는 것으로 조사되었다. 파트2에서는 우리나라의 대표적 주택형태인 아파트, 단독주택, 다세대주택의 실내공기질을 조사하고 실내 오염물질 농도와 환경 영향 인자간의 상관성을 통계적으로 살펴보았다.

주요어 : 다공성물질, 흡착, 표면개질, 공기 오염물질, 실리카, 그라핀, 휘발성유기화합물

학 번 : 2012-30876