

Adsorption of acetaldehyde at room temperature in a continuous system using silica synthesized by the sol-gel method

Moon Il Kim, Suhyun Kim, Choong-sun Lim, and Bongkuk Seo[†]

Center for Chemical Industry Development, Korea Research Institute of Chemical Technology, Ulsan 44412, Korea
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Abstract—Volatile organic compounds (VOCs) are hazardous chemicals present in outdoor and indoor air. They can be odorous and cause human health problems even at very low concentrations. Therefore, regulations on VOC gas emission are becoming stricter every year. Acetaldehyde is a VOC gas that not only has a very stinging smell but can also harm the human body by inhalation. Representative commercial adsorbents are activated carbon and silica gel. These materials feature a large surface area, which is directly related to the number of adsorption sites. In this study, a silica xerogel was synthesized by sol-gel method. The new material was tested for the adsorption of acetaldehyde in a continuous bed system, and its performance was compared to those of commercial silica gel and activated carbon. The physical properties of the samples were studied by BET analysis. Silica xerogel was characterized by XRD, FT-IR, and ²⁹Si MAS NMR. The inlet and outlet concentrations of the VOC gas were measured from adsorption test tubes using a VOC detecting monitor. The synthesized silica xerogel presented a larger surface area and number of functional groups than the commercial silica gel, leading to improved adsorption performance and selectivity.

Keywords: VOC Adsorption, Silica, Sol-gel, Xerogel, Acetaldehyde

INTRODUCTION

The reduction and removal of volatile organic compounds (VOCs) represent important challenges toward environmental and human health improvement [1,2]. Humans are highly exposed to indoor VOCs as a large number of materials are used in construction, automobiles, and the household include polymer- and hydrocarbon-based chemicals to achieve the required strength, light-weight, and durability. These VOCs are not only harmful but also odorous, and can be easily detected in new houses, automobiles, and households. Many countries have put in place regulations to reduce VOC emissions inside automobiles and houses. To fulfill such regulations, much research has been carried out with two main purposes: manufacturing materials with less VOCs and removing the already released VOCs.

A variety of VOC materials are present inside automobile vehicles: head linings, door trims, crash pads, wirings, dash isolation pads, seats, luggage mats, floor carpets, package trays, etc. Most of these VOCs are odorous, being mostly BTX (benzene, toluene, xylene) or aromatic, alcohol, glycol, aldehyde, amine, and ether compounds. Acetaldehyde is an odorous VOC gas, with high volatility and a very stinging smell. As with any other VOC, inhalation of acetaldehyde is harmful for the human body [3,4].

The existing methods to remove VOC materials are combustion, oxidation, adsorption, condensation, and absorption. Oxidation and combustion are VOC-reducing techniques that produce different compounds. These methods usually require additional reac-

tants and high temperatures, and are thus suitable for application in power plants, steel refineries, and petrochemical factories for emission control. Other approaches toward VOC removal are condensation, absorption, and adsorption, which can retrieve the removed VOCs later. These methods are simpler than the combustion or oxidation methods and can thus be easily applied in industrial fields. Condensation is a very efficient method to remove VOCs when their concentration is over 1% [5]. On the other hand, the adsorption method is very effective when the concentration of VOCs is <1%, requiring not only low energy and cost, but also offering great flexibility for application in a variety of systems [6]. Approximately, only 10% of the industry uses adsorption methods for VOC reduction; however, the extent of adsorbent usage is on the rise. Moreover, the number of studies on the development of industrial adsorbents for VOC removal has recently increased, as the regulations to limit VOC emissions have become more and more strict [7].

Adsorbents to remove VOCs or polluting substances have been studied by many researchers, including those in the field of nanotechnology. Such adsorbents include clay materials [8,9], zeolites [7,10], activated carbon [11], silica gels [12,13] and metal organic frameworks (MOFs) [14]. These materials can adsorb VOCs physically, chemically, or physico-chemically. The most widely used adsorbent is activated carbon, owing to its large surface area and low cost. Also, activated carbon exhibits microporosity, which can lead to good adsorption performance [11]; however, it has low thermal and chemical stability, and also low reusability. Due to the lack of chemical functional groups and the high surface area of activated carbon, only physical adsorption can occur, leading to low selectivity and efficiency, and short lifetimes. Zeolites are also good adsorbents due to their high porosity; however, they are ten times

[†]To whom correspondence should be addressed.

E-mail: bksea@kRICT.re.kr

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more expensive than activated carbon and very sensitive to moisture [9]. Clay materials have become good alternatives due to their low cost and high porosity, although their performance is inconsistent. Certain modifications, such as acid treatments and intercalation, have been reported to improve the performance of clays [10,11]. Silica gels have good thermal, mechanical, and vapor stability, high surface area with microporosity, and various functional groups, such as silanols and siloxanes. Due to their high surface area, they present high adsorption capacity that can lead to physical adsorption. In addition, due to the presence of functional groups, chemical adsorption can also occur, leading to selective adsorption. Therefore, silica gels are promising adsorbents with great adsorption performance and long lifetimes [15].

One of the most common approaches to synthesizing adsorbents and catalysts with high surface area and stable activity is the sol-gel method [15-18]. The sol can be obtained from monomers by hydrolysis and polymerization. When the sol is synthesized with an acid accelerator, gelation occurs and a gel is obtained. The drying conditions determine whether an aerogel or a xerogel is formed. Aerogels are obtained when drying is carried out under supercritical conditions after gelation. Xerogels are synthesized under conventional drying conditions. Both aerogels and xerogels present high surface areas, but that of aerogels is larger since the particle network structure of aerogels does not collapse as easily as that of xerogels. However, the synthesis of xerogels may be more desirable commercially because the synthesis of aerogels requires complex drying conditions which leads to high maintenance [13].

In the present work, a silica xerogel was synthesized and applied for acetaldehyde adsorption in a continuous system. The performance of the xerogel was compared to that of commercial activated carbon and silica gel in terms of their adsorption efficiency, adsorption capacity, and lifetime.

EXPERIMENTAL

1. Synthesis of the Silica Xerogel by the Sol-gel Method

A silica xerogel was synthesized following the method previously reported by Arenas et al. [19] with some modifications. The sol-gel method is based on the hydrolysis and polycondensation of tetraethylorthosilicate (TEOS) in acidic medium. TEOS (22 mmol) was dissolved in 5 mL of acetone. An acidic solution containing 5 mL of acetic acid, 0.1 mL of HCl, and 1.6 mL of doubly distilled water was then added to the above solution. After stirring for 5 min, the mixture was left at ambient temperature without sealing for two weeks for gelation and drying. After drying, the sample was ground using a mortar. Then, it was washed several times with a mixture of distilled water and ethanol (1 : 1), and dried in an oven at 100 °C overnight.

2. Adsorbent Characterization

The structure of the silica xerogel was investigated by X-ray diffraction (XRD), Fourier transform infrared (FT-IR), and silicon-29 magic-angle spinning-nuclear magnetic resonance (^{29}Si MAS NMR) spectroscopy. The powder XRD patterns were recorded on a Rigaku Ultima IV diffractometer using CuK radiation (40 kV, 40 mA) with a step size of $\Delta 2\theta=0.02^\circ$ and 4 seconds per step. The FT-IR spectra were acquired on a Thermo Nicolet 6700 spectrophotometer with

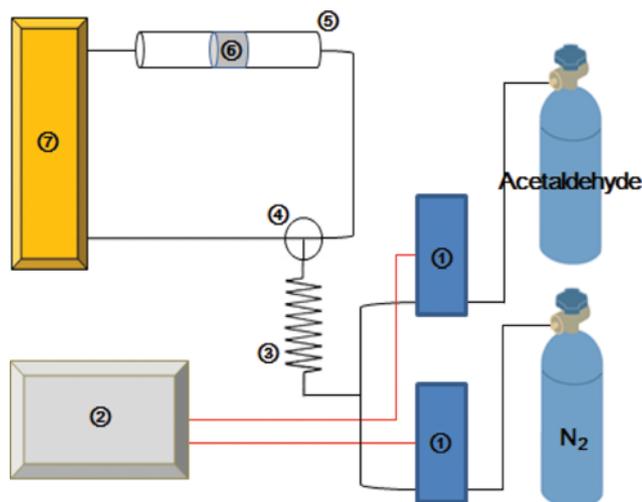


Fig. 1. Schematic apparatus for continuous adsorption tests.

- | | |
|------------------------|-------------------------|
| ① Mass flowmeter | ⑤ Adsorption tube |
| ② Mass flow controller | ⑥ Adsorbent bed |
| ③ Mixing coil | ⑦ VOC detector, monitor |
| ④ 3-Way valve | |

a resolution of 4 cm^{-1} . ^{29}Si MAS NMR data were acquired on a 600 MHz solid state NMR spectrometer (^{29}Si INOVA Agilent Technologies, U.S.A.) at the KBSI Western Seoul Center. The rotor spinning speed was 22 and a $2.2\ \mu\text{s}$ pulse was used with a repetition time of 40 s. The textural properties of the samples were analyzed by recording the N_2 adsorption isotherms at 77 K using a Brunauer-Emmett-Teller (BET) apparatus (Micromeritics ASAP 2420). Before gas sorption analysis, the materials were pretreated for 12 h at 120 °C under vacuum. The specific surface area was determined using the BET model equation.

3. Adsorption Tests

To compare the performance of the adsorbents, such as their lifetime and adsorption capacity, adsorption tests were carried out in a continuous system. A schematic of the adsorption test apparatus is shown in Fig. 1. The tested adsorbents were the synthesized silica xerogel, commercial silica gel (Sigma-Aldrich), and commercial activated carbon (Gaya Co., Ltd., S. Korea). The adsorbents (1 g) were loaded in a test tube with a diameter of 1/2 inch. The size of the adsorbents was controlled with a 60-100 mesh to prevent pressure drops. The test gas was a mixture of acetaldehyde and nitrogen with a starting acetaldehyde concentration of 200 ppm. The concentration of acetaldehyde was then controlled with a nitrogen gas line. A mass flow controller (MFC) was used to control the concentration of feed gases. A mixing coil was set after the MFCs for better mixing. After the mixing coil, the gas mixture passed through a three-way valve: one way to the VOC detector to accurately measure the initial concentration of feed gas and the other one to the test tube with the adsorbent bed. After the feed gas concentration was checked, the three-way valve was set to allow the feed gas to travel through the adsorbent. The acetaldehyde remaining after the adsorbent bed was detected using a VOC monitor (mini RAE 3000, Honeywell). The gas concentration was measured every 60 s. The total mass flow was set to 500 mL min^{-1} since the pump inside the VOC monitor pulled the gas at that flow rate.

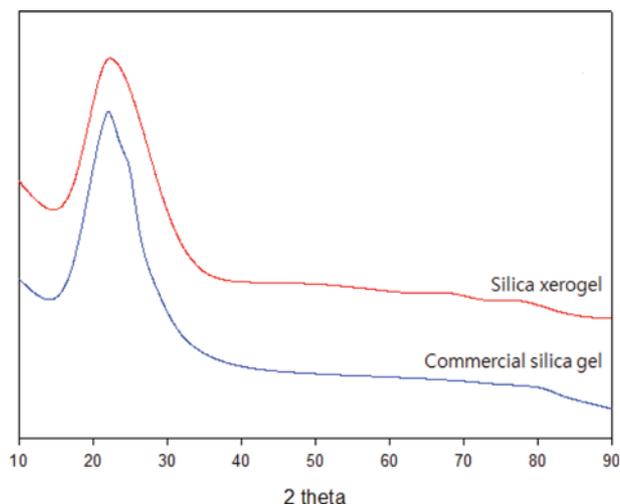


Fig. 2. X-ray diffraction patterns of the synthesized silica xerogel and commercial silica gel.

RESULTS AND DISCUSSION

1. Characterization of Adsorbents

Fig. 2 shows the XRD patterns of the synthesized silica xerogel and commercial silica gel. The XRD patterns exhibit a peak at $2\theta=22^\circ$, which is assigned to amorphous SiO_2 . Multiple washings with a mixture of distilled water and ethanol seemed to be efficient in removing impurities, resulting in a smooth pattern with a unique band. Moreover, the broadness of the peak confirmed the absence of crystalline silica [20].

Fig. 3 shows the FT-IR spectra of both the commercial silica gel and synthesized silica xerogel in the range of $400\text{--}4,000\text{ cm}^{-1}$. Both

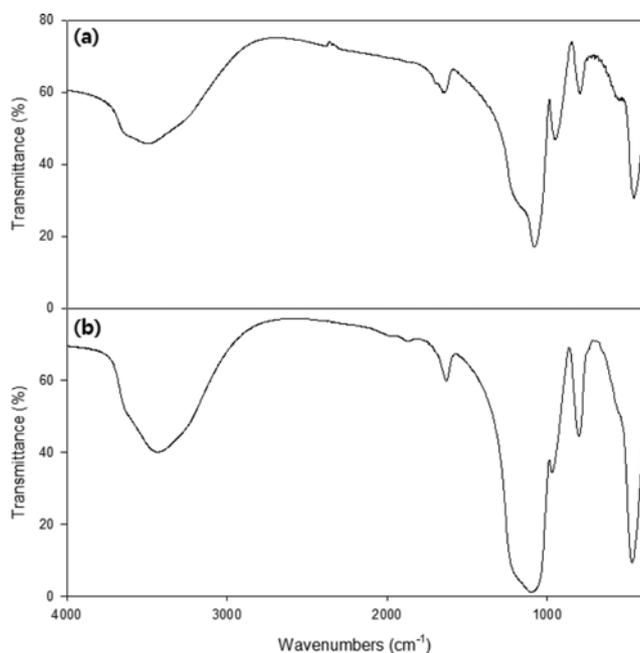


Fig. 3. FT-IR spectra of silica adsorbents: (a) synthesized silica xerogel and (b) commercial silica gel.

samples show the typical bands for the various vibrations of silanol and siloxane groups in a solid network. The existence of silanol (Si-OH) groups was confirmed on the basis of previously published data. It has been reported that the large broad band at around $3,450\text{ cm}^{-1}$ indicates overlapping of the O-H stretching bands of water molecules hydrogen-bonded to the surface silanol moieties. [21] At $1,653\text{--}1,324\text{ cm}^{-1}$, deformation of the vibrations is observed for the adsorbed water molecules due to the presence of surface silanol groups, which are hydrophilic in nature [22]. The Si-O stretching vibration of silanol groups appears at around 960 cm^{-1} [23]. In the same manner, siloxane (O-Si-O) groups were identified as follows. Intense peaks were observed for the Si-O covalent bond vibrations in the range of $1,200\text{--}1,000\text{ cm}^{-1}$. In this range, two specific peaks were observed, which correspond to the transversal optical modes ($1,095\text{--}1,089\text{ cm}^{-1}$) and longitudinal optical modes ($1,200\text{ cm}^{-1}$) of the Si-O-Si asymmetric stretching vibrations [24]. The remaining peaks at around 800 cm^{-1} and 470 cm^{-1} represent the symmetric vibration of Si-O-Si and its bending mode, respectively [21,25]. In summary, silica xerogel was successfully synthesized with a variety of functional groups that will contribute to improve the selective adsorption performance of this material.

To assess the number of silanol and siloxane groups, ^{29}Si MAS NMR characterization of both the commercial and synthesized silica gels was carried out. The corresponding ^{29}Si MAS NMR spectra are shown in Fig. 4. The signals at around -110 ppm , -102 ppm , and -90 ppm were assigned to Q_4 , Q_3 , and Q_2 , respectively. The subscript numbers represent the number of Si neighboring-atoms, where Q_4 denotes $(\text{SiO})_4\text{*Si}$, Q_3 corresponds to $(\text{SiO})_3\text{*SiOH}$, and Q_2 refers to $(\text{SiO})_2\text{*Si(OH)}_2$. It was revealed that the synthesized silica xerogel possesses a larger number of functional groups than the commercial silica gel. Fig. 5 shows the ^{29}Si NMR spectra after deconvolution, and the relative areas of each peak for both adsorbents are summarized in Table 1. It can be concluded that silica xerogel has a larger number of silanol groups (Q_2 and Q_3) than the commercial sample. In sum, it was confirmed that the synthesized xerogel presents more functional groups than the commercial silica gel, which may lead to enhanced selective adsorption of

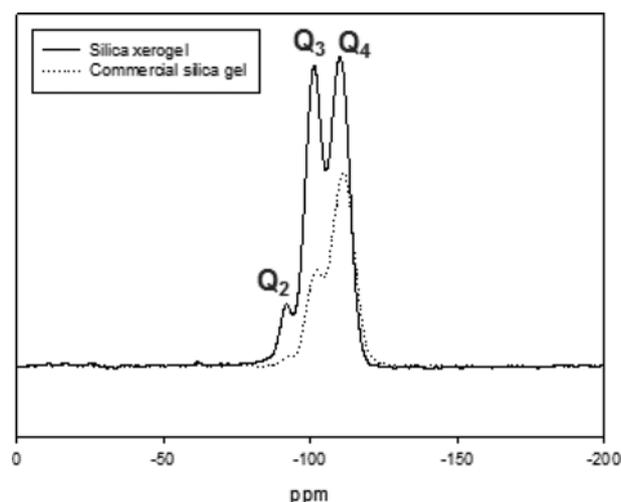


Fig. 4. ^{29}Si MAS NMR spectra of the synthesized silica xerogel and commercial silica gel.

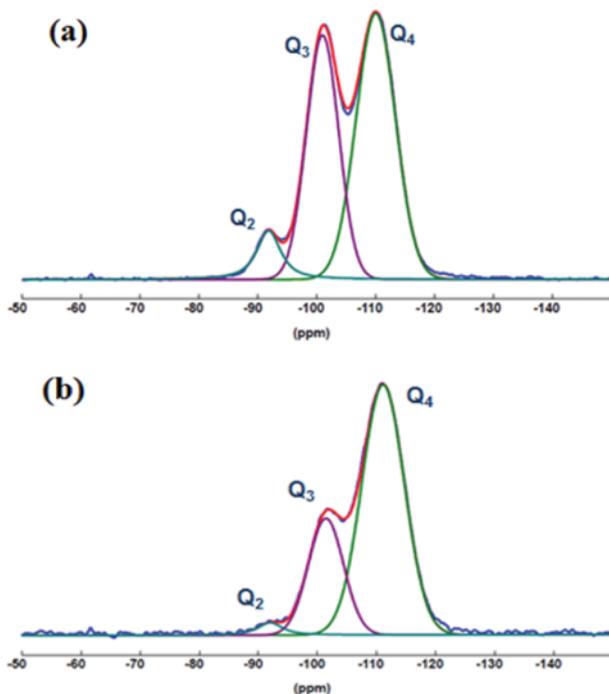


Fig. 5. ^{29}Si NMR spectra of (a) silica xerogel and (b) commercial silica gel after deconvolution.

VOCs [12].

Table 2 shows the textural properties of the adsorbents from the BET surface area analysis. The BET surface area of the synthesized silica xerogel was $662.9 \text{ m}^2 \text{ g}^{-1}$, whereas that of the commercial silica gel was only $474.3 \text{ m}^2 \text{ g}^{-1}$. Such a large surface area indicates that the silica network was not destroyed during the drying procedure. Silica networks typically collapse during drying processes in xerogel synthesis due to the high temperatures used to evaporate the solvent(s). However, it seems that drying at ambient temperature prevented said collapse as the solvent was slowly removed, maintaining the original network structure.

2. Performance of Adsorbents for Acetaldehyde Adsorption

2-1. Adsorption of Acetaldehyde with Different Adsorbents

Since the threshold limit value of acetaldehyde is 25 ppm, the acetaldehyde concentration was set just under 25 ppm for the adsorption tests. The gas input was controlled by the MFC at a total

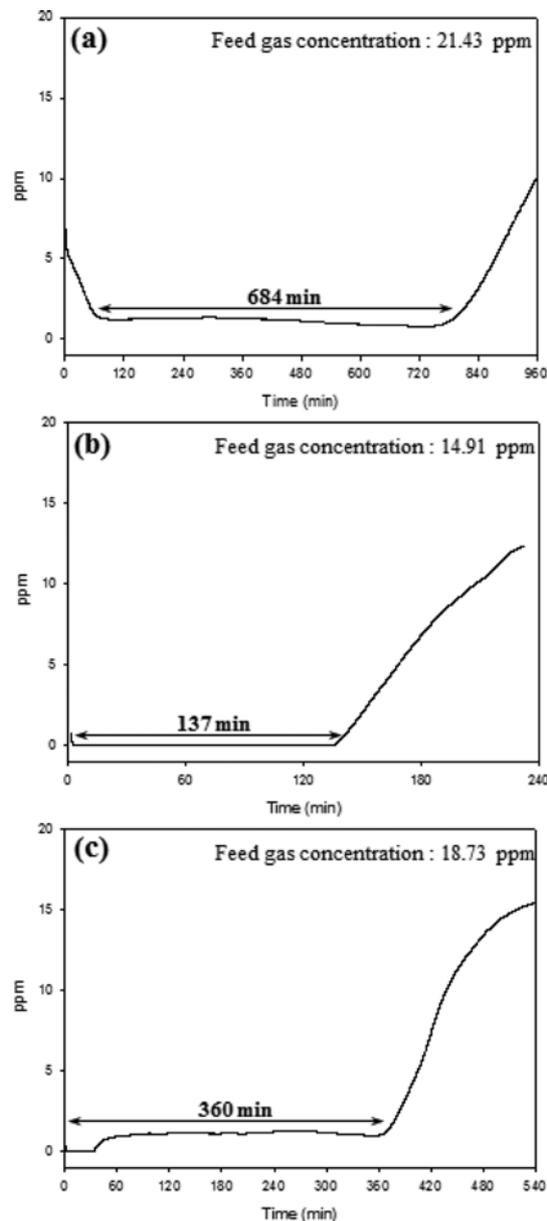


Fig. 6. Changes in acetaldehyde concentration during adsorption tests in a continuous system using different adsorbents: (a) silica xerogel, (b) commercial silica gel (Sigma-Aldrich), and (c) commercial activated carbon (Gaya Co. Ltd., S. Korea).

Table 1. Relative areas of the signals in the ^{29}Si NMR spectra of silica xerogel and commercial silica gel

Sample	Synthesized silica xerogel			Commercial silica gel		
	Chemical shift (ppm)	Relative area (%)		Chemical shift (ppm)	Relative area (%)	
	-100	52.5		-110	70.2	
	-101	39.6		-101	27	
	-92	7.9		-92	2.8	

Table 2. BET Surface area, micropore volume (V_{mp}) and pore diameter (D_p) of adsorbents investigated

Sample	Surface area ($\text{m}^2 \text{ g}^{-1}$)	V_{mp} (mL g^{-1})	D_p (\AA)
Silica xerogel	662.9	0.0883	27.18
Commercial silica gel (Sigma-Aldrich)	474.3	0.9356	61.97
Commercial activated carbon (Gaya Co. Ltd., S. Korea)	1039.6	0.0884	30.05

Table 3. Acetaldehyde adsorption with different adsorbents

Sample	Lowest concentration segment			Removal efficiency (%), $((C_{\text{Feed}} - C_{\text{Lowest}})/C_{\text{Feed}}) \times 100$
	Time (min)	Avg. conc. (ppm)	Adsorbed amount (mL)	
Silica xerogel	684	1.103	6.953	94.85
Comm. silica gel	137	0.020	1.050	99.87
Comm. act. carbon	360	0.979	3.196	94.77

flow rate of 500 mL min^{-1} with 50 mL min^{-1} of 200 ppm acetaldehyde and 450 mL min^{-1} of N_2 . The feed gas concentration was accurately determined before passing through the adsorbent bed using a three-way valve, since the aldehyde concentration can vary upon mixing both feed gases. Fig. 6 shows how the concentration of acetaldehyde changed during the adsorption tests using different adsorbents in the continuous system. All the samples exhibited a similar pattern, which included a 'lowest concentration' plateau, at which the adsorbent is displaying its best performance. The data corresponding to these lowest concentration segments are shown in Table 3. The amount adsorbed throughout these plateaus was calculated using the following equation: Adsorbed amount throughout the lowest concentration segment = (Actual feed concentration - Average concentration during the lowest concentration segment) \times Total flow rate \times Duration of the lowest concentration segment.

The data in Fig. 6 and Table 3 demonstrate that the silica xerogel displays the longest lowest concentration segment (684 min). Upon comparison with the commercial silica gel, the silica xerogel presented a lifetime ~5 times longer. This observation may be the result of the increased number of silanol and siloxane groups in the synthesized silica xerogel sample [12]. The duration of the lowest concentration segment using activated carbon was much shorter than that of the silica xerogel, even though activated carbon displays a higher surface area. It has been reported that, due to the absence of functional groups on the surface activated carbon, it not only adsorbs the targeted VOC but also other gases such as nitrogen as well in ambient conditions [9]. Due to its tendency to adsorb every gas, it displays shorter lifetimes than the silica xerogel.

2-2. Adsorption of Acetaldehyde at Different Concentrations Using Silica Xerogel

Additional adsorption tests at different acetaldehyde concentrations were carried out using the synthesized silica xerogel. The initial concentration of acetaldehyde for the parameter tests was 10, 20, and 40 ppm, which changed throughout the tests, as shown in Fig. 7 for each feed concentration. The results for the lowest concentration segments are also shown in Table 4. The lifetime of the lowest concentration segment for the feed gas concentrations of 10, 20, and 40 ppm was 950, 684, 306 min, respectively. The duration of the lowest concentration segment for the 10 ppm gas feed was not twice as that of 20 ppm gas feed. This might be due to slow adsorption rates at low concentrations, which result in the lowest concentration point being reached much later than when using 20 or 40 ppm of the feed gas. This effect is also present in the total amount adsorbed when using a concentration of 10 ppm, for which the smallest adsorption capacity was observed. The amount of acetaldehyde adsorbed was over 6 mL at concentrations ≥ 20 ppm. The removal efficiency increased with the increas-

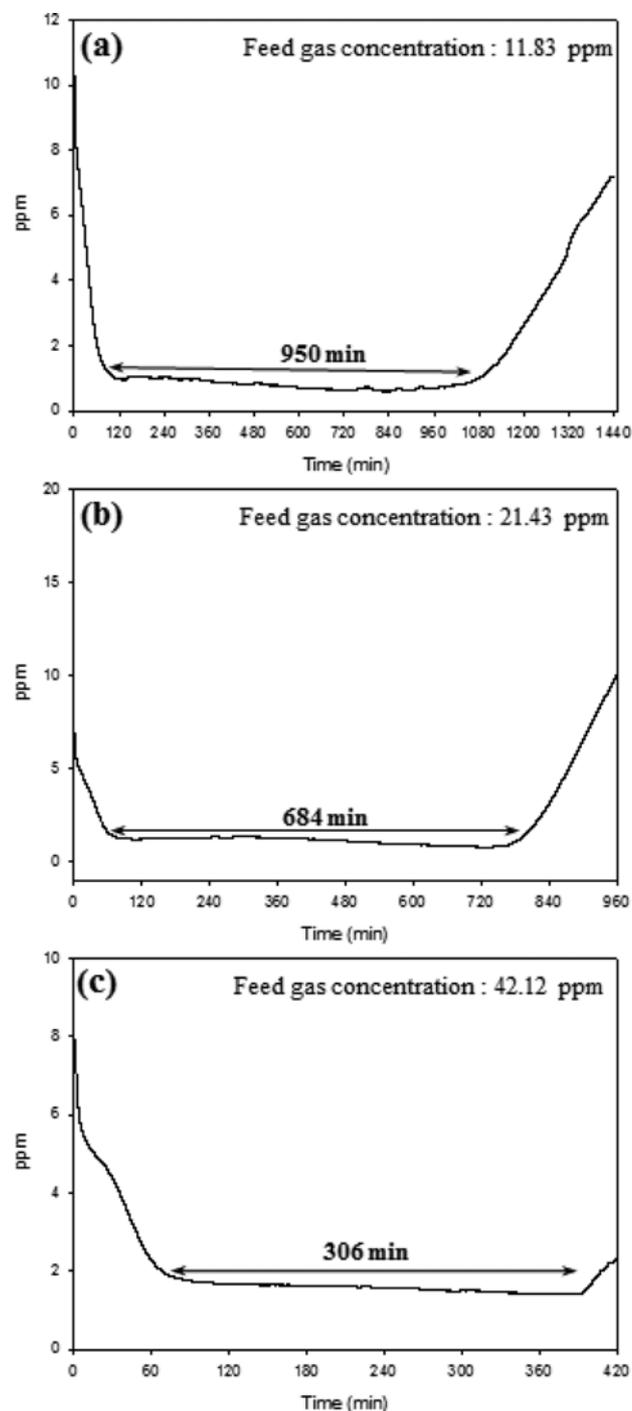
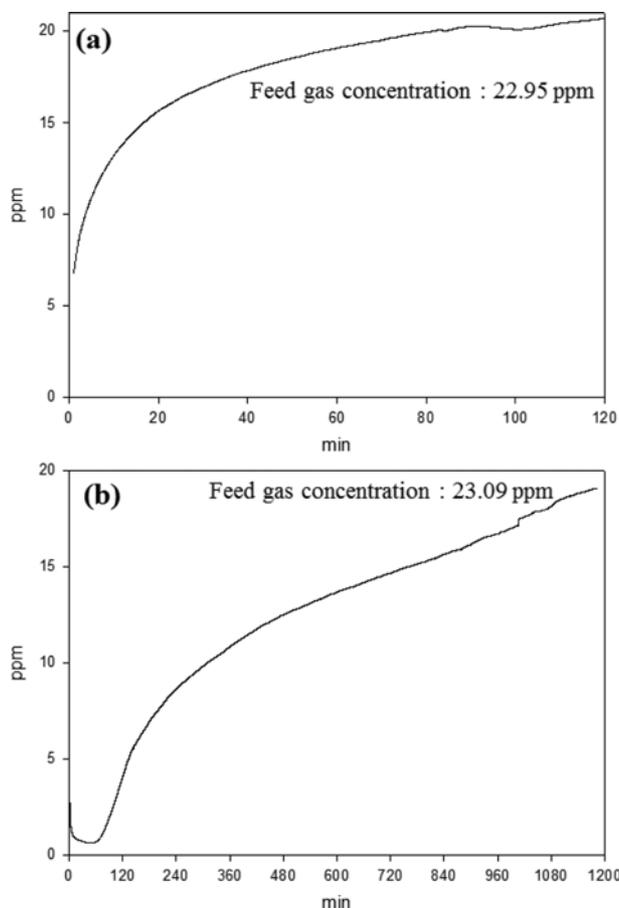


Fig. 7. Changes in acetaldehyde concentration during adsorption tests using the silica xerogel at different feed concentrations: (a) 10 ppm, (b) 20 ppm, and (c) 40 ppm.

Table 4. Acetaldehyde adsorption at different feed concentrations using the silica xerogel

Feed concentration (ppm)	Lowest concentration segment			Removal efficiency (%), $((C_{Feed} - C_{Lowest})/C_{Feed}) \times 100$
	Time (min)	Avg. conc. (ppm)	Adsorbed amount (mL)	
10	950	0.801	5.239	93.23
20	684	1.103	6.953	94.85
40	306	1.562	6.205	96.29

**Fig. 8. Changes of acetaldehyde concentration during adsorption test using re-used silica xerogel by (a) calcination and (b) washing and drying.**

ing feed concentration. It can be concluded that the silica xerogel synthesized in this study showed a satisfactory lifetime, adsorption capacity, and removal efficiency regardless of the concentration of the target VOC gas.

2-3. Re-usability of Silica Xerogel on Adsorption of Acetaldehyde

Re-usability is a crucial aspect in the industrial field from the economical aspect. Usually, acetaldehyde on the adsorbent can be removed by oxidation forming carbon dioxide and water or carbon monoxide [26,27]. However, acetaldehydes cannot be completely degraded, and could also result in unwanted harmful chemicals, such as nitrogen dioxide and ozone. Furthermore, they can be hard to apply at industrial scale, due to additional cost on the device for the appliance. For the re-usability test, silica xerogel was regenerated by heating treatment and washing method in this work,

Table 5. Physical properties of silica xerogel with different regeneration methods

Sample	Surface area (m^2/g)	V_{mp} (ml/g)	D_p (\AA)
Fresh silica xerogel	662.9	0.0883	27.18
Calcination	147.8	0.0312	31.09
Washing	522.1	0.0839	25.20

which could be easily adapted industrially.

Silica xerogel saturated with acetaldehyde was treated with two methods: heating by calcination and washing with aqueous ethanol solution, separately. For the heating method, silica xerogel saturated with acetaldehyde was calcined at 550 °C for 6 h. Silica xerogel treated by washing was dried at 100 °C before the adsorption test. The adsorption test was done using 20 ppm acetaldehyde.

Adsorption test results using re-used adsorbent are described in Fig. 8. Both regenerated silica xerogel showed very less performance; adsorbent regenerated by washing showed about 85 minutes of lowest concentration section, and with the calcination showing no time section at all. To check out the changes on surface area of the adsorbent, BET analysis was done for both regenerated silica xerogel, and they are summarized in Table 5. Surface area of both samples decreased, and the sample with heat treatment was largely dropped. It has been reported that pore volume and the surface area of silica gels can be decreased by calcination at high temperature [28,29], which can be proved by BET analysis result. Also, it has been found that the washing method cannot recover the adsorption site, completely. Therefore, washing method or heating treatment, which can be easily apply in industrial field, of the used silica xerogel is not well suitable for the recovery of the adsorbent performance. However, other methods to regenerate silica adsorbents, such as oxidation, are still available. Thus, more research on silica xerogel recovery for application on an actual industrial field will be needed.

CONCLUSION

A silica xerogel was successfully synthesized at room temperature with a large surface area. The silica synthesized by the sol-gel method displayed higher surface area than the commercial silica gel. The silica xerogel also showed an increased number of silanol and siloxane groups compared to the commercial material. The synthesized xerogel exhibited better performance toward the adsorption of acetaldehyde than other commercial adsorbents, with almost twice the lifetime and more than twice the adsorption capacity than activated carbon at low acetaldehyde concentrations. The large number of silanol and siloxane groups in the silica xerogel

led to selective adsorption of acetaldehyde. The silica xerogel also displayed good adsorption performance at high acetaldehyde concentrations. However, it cannot be regenerated by simple washing method or calcination, which requires further study for industrial application.

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