Indoor formaldehyde removal over CMK-3

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Abstract
The removal of formaldehyde at low concentrations is important in indoor air pollution research. In this study, mesoporous carbon with a large specific surface area was used for the adsorption of low-concentration indoor formaldehyde. A mesoporous carbon material, CMK-3, was synthesized using the nano-replication method. SBA-15 was used as a mesoporous template. The surface of CMK-3 was activated using a 2N H₂SO₄ solution and NH₃ gas to prepare CMK-3-H₂SO₄ and CMK-3-NH₃, respectively. The activated samples were characterized by N₂ adsorption-desorption, X-ray diffraction, and X-ray photoelectron spectroscopy. The formaldehyde adsorption performance of the mesoporous carbons was in the order of CMK-3-NH₃ > CMK-3-H₂SO₄ > CMK-3. The difference in the adsorption performance was explained by oxygen and nitrogen functional groups formed during the activation process and by the specific surface area and pore structure of mesoporous carbon.

Keywords: low-concentration formaldehyde, mesoporous carbon, sulfuric acid, ammonia, activation, adsorption

Introduction
Currently, people spend more than 80% of their daily life indoors and are exposed to serious health risks due to indoor air pollution. In particular, the increased air-tightness required for energy saving results in the accumulation of pollutants in less-ventilated indoor air. Sick building syndrome causing throat and nasal pains, headache, nausea, and vomiting due to indoor air pollution has become an important social issue with the increasing desire to improve the quality of life [1-3].

Formaldehyde is a representative indoor pollutant that is emitted from indoor furniture paint and floor materials. Formaldehyde has been categorized as a group 1 carcinogen by the International Agency for Research on Cancer [4]. Therefore, technology for removing formaldehyde is of great importance [5].

Adsorption, scrubbing, and advanced oxidation have been applied to remove volatile organic compounds, such as formaldehyde. In particular, adsorption using activated carbon is a method used most widely for removing formaldehyde [6]. Although the adsorption performance of activated carbon is excellent, it is not very efficient for the adsorption of polar species, such as formaldehyde.

Therefore, research is being carried out to develop more efficient adsorbents for formaldehyde [7].

Recently, the synthesis and application of ordered mesoporous carbons with a variety of structures, e.g., CMK-1, CMK-3, and CMK-5, have attracted considerable attention [8-11]. These ordered mesoporous carbons have been synthesized by carbonizing mesoporous silica materials, such as MCM-48, SBA-15, and KIT-6, and then by removing the silica template. Ordered mesoporous carbon is expected to have an extensive potential in a range of applications because of the uniform pore size, large specific surface area, and large pore volume [12]. These materials are considered to have a potential for applications to other fields, such as heterogeneous catalysis and host-guest chemistry [13-16]. In particular, CMK-3, based on SBA-15, which is easy to synthesize, is expected to be useful not only as an adsorbent but also as a catalyst substrate [12].

In this study, CMK-3 was applied for the first time to the adsorption of formaldehyde. The effect of modifying the surface of CMK-3 via a range of activations to improve the formaldehyde removal efficiency was evaluated.

Experimental details
Synthesis of CMK-3
An ordered mesoporous carbon, CMK-3, was prepared using the nano-replication method. Mesoporous silica
SBA-15 was used as a template. A carbon precursor solution was prepared by dissolving 1.25 g of sucrose in a mixture containing 4 g of deionized water and 0.14 g of H$_2$SO$_4$. The solution was allowed to infiltrate into the mesopores of the silica template. The mixture was dried at 100°C for 6 h. The impregnation and drying procedures were repeated twice using 66% sucrose. The carbonization was carried out at 900°C and allowing ammonia gas to flow through the reactor at a flow rate of 50 ml/min for 2 h. The reactor was purged for another 1 h with nitrogen gas at a flow rate of 50 ml/min. CMK-3 was obtained by removing the silica matrix using an HF solution.

Ammonia and sulfuric acid treatments were applied to upgrade the characteristics of CMK-3. The ammonia treatment was performed by inserting CMK-3 into a reactor maintained at 900°C and allowing ammonia gas to flow through the reactor at a flow rate of 50 ml/min for 2 h. The reactor was purged for another 1 h with nitrogen gas at a flow rate of 50 ml/min. CMK-3, which was treated with ammonia in this way, is referred to as CMK-3-NH$_3$.

The method of the sulfuric acid treatment of CMK-3 is as follows: CMK-3 was immersed in a 2N sulfuric acid solution prepared by using 95% sulfuric acid. The solution was stirred for 3 h at room temperature. The solution was then filtered, and the filtered sample was immersed in 100 g of distilled water and stirred for 1 h. This filtration and washing procedure was repeated at least ten times to neutralize the sample. The washed sample was dried for 24 h in an oven maintained at 110°C. The CMK-3 treated with sulfuric acid is referred to as CMK-3-H$_2$SO$_4$.

Results and discussion
Characterization of mesoporous carbons
X-ray diffraction [XRD] was carried out in reflection mode using a Rigaku D/MAX-2200 Ultima diffractometer (Rigaku International Corporation, Tokyo, Japan) equipped with Cu Kα radiation at 30 kV and 40 mA. N$_2$ adsorption-desorption isotherms were collected on a Micromeritics Tristar system (Micromeritics Instrument Corporation, Chiba, Japan) at liquid N$_2$ temperature. The specific BET surface area was calculated from the adsorption branches in the relative pressure (P/P$_0$) range of 0.05 to 0.20. The pore size distribution curves were obtained from the adsorption branches using the BJH method.

X-ray photoelectron spectroscopy [XPS] measurements were performed using an AXIS Nova spectrometer (Kratos. Inc., NY, USA). A monochromatic Al Kα (1,486.6 eV) X-ray source and 40 eV of analyzer pass energy were used under ultra-high vacuum conditions (5.2 × 10$^{-9}$ Torr).

Adsorption of formaldehyde
The adsorption experiments were carried out using the method described in the literature [17]. The 100-ppm formaldehyde produced by Union Inc. was used in this study. A 10-L aluminum bag (to prevent oxidation by sunlight) was cleaned with N$_2$ gas and emptied using a vacuum pump. After introducing formaldehyde into the bag, N$_2$ gas was added to adjust the formaldehyde concentration to 1 ppm. Subsequently, 0.07 g of mesoporous carbon, which had been dried in advance for 24 h in an oven maintained at 100°C to remove the influence of moisture, was inserted into the aluminum bag. The temperature was controlled at 30°C using an incubator during the adsorption process to avoid any temperature dependency [17]. The sample bags were agitated in a shaking incubator to promote gas-solid mixing.

The amount of formaldehyde adsorbed at 0, 10, 40, and 80 min was measured using a formaldehyde analyzer (4000Series; Woori Industrial System Co., Ltd., Cheongwon-gun, South Korea).

Table 1 lists the physical properties of mesoporous carbon used in this study. The specific surface area of CMK-3 was 1,178 m$^2$/g. The specific surface area decreased slightly to 1,002 m$^2$/g after a treatment with sulfuric acid, whereas it increased considerably to 1,663 m$^2$/g upon a treatment with ammonia. Figure 1 shows the nitrogen sorption isotherms and pore size distributions of mesoporous carbon. Figure 2a shows the nitrogen sorption isotherms for CMK-3, CMK-3-H$_2$SO$_4$, and CMK-3-NH$_3$. All the samples showed typical type IV isotherms of mesoporous materials under a relative pressure (P/P$_0$) of 0.5. Table 1 shows that CMK-3 has mesopores with a pore size of 3.8 nm. These mesopores were maintained after a treatment with sulfuric acid. When CMK-3 was treated with ammonia, the mean pore size decreased to 3.1 nm. Treatment with ammonia is a high-temperature (900°C) process that generates micropores causing a large increase in surface area and a decrease in average pore size. On the other hand, most of the mesoporous CMK-3 were maintained after the ammonia treatment.

Table 2 lists the elemental surface compositions obtained by XPS. CMK-3-H$_2$SO$_4$ showed higher C and O contents than CMK-3, whereas CMK-3-NH$_3$ had lower C and O contents than CMK-3. N was detected in CMK-3-NH$_3$, but not in CMK-3. This suggests that a sulfuric acid treatment and ammonia treatment have added oxygen and nitrogen functional groups, respectively, on the CMK-3 surface.
Figure 3 shows the O1s and N1s spectra obtained from XPS. The O1s spectra (Figure 3a) showed four peaks even though the intensity of each peak was dependent on the treatment method. Generally, the peaks appeared at the binding energy levels of 531.1 (± 0.5), 532.8 (± 0.5), 535.1 (± 0.5), and 537.6 (± 0.5) eV, representing C-OH, C=O, O₃, and O₄, respectively [18]. The C-OH peak was shown to increase dramatically after the sulfuric acid treatment. The N1s spectrum was detected only for CMK-3-NH₃ (Figure 3b). N1s peaks were observed at two binding energy levels. The peaks appearing at 399.2 (± 0.5) and 400.9 (± 0.5) eV represent atomic N and pyridine-like N, respectively [19].

![Figure 1 Adsorption-desorption isotherms and pore size distribution](image1)

![Figure 2 XRD patterns of CMK-3, CMK-3-H₂SO₄, and CMK-3-NH₃ samples](image2)

**Table 1** Physicochemical properties of various CMK-3 materials

| Sample      | Specific surface area (m²/g) | Total pore volume (cm³/g) | Average pore diameter (nm) | Micropore area (m²/g) | Micropore volume (cm³/g) |
|-------------|------------------------------|----------------------------|---------------------------|-----------------------|--------------------------|
| CMK-3       | 1178                         | 1.28                       | 3.8                       | 142                   | 0.05                     |
| CMK-3-H₂SO₄ | 1002                         | 1.14                       | 3.8                       | 93                    | 0.03                     |
| CMK-3-NH₃   | 1633                         | 1.55                       | 3.1                       | 394                   | 0.16                     |
Adsorption of formaldehyde

Figure 4 shows the results of the formaldehyde adsorption experiments using CMK-3, CMK-3-H$_2$SO$_4$, and CMK-3-NH$_3$. Adsorption occurred most rapidly in the first 10 min and then slowed down gradually. Without treatment, CMK-3 showed a high adsorption efficiency $>50\%$ owing to its large specific surface area. CMK-3-H$_2$SO$_4$ showed slightly improved adsorption performance compared to CMK-3 despite its smaller specific surface area than CMK-3, which was attributed to the highest surface O concentration resulting from an increase in oxygen functional groups. Lee et al. [20] reported that the increase in oxygen functional groups on sludge char through activation increased the formaldehyde adsorption efficiency, which is in good agreement with the present results.

CMK-3-NH$_3$ showed the highest formaldehyde adsorption performance. Kim et al. [17] examined the effect of the addition of amine groups to mesoporous

| Sample          | Atomic surface concentration obtained by XPS (%) |
|-----------------|-----------------------------------------------|
|                 | C    | O    | N    |
| CMK-3           | 96.67 | 2.11 | -    |
| CMK-3-H$_2$SO$_4$ | 97.18 | 2.82 | -    |
| CMK-3-NH$_3$    | 94.49 | 1.43 | 3.66 |

Figure 3 XPS spectra of CMK-3, CMK-3-H$_2$SO$_4$, and CMK-3-NH$_3$ samples: (a) O1s spectrum and (b) N1s spectrum.
materials and reported that the addition of amine groups could enhance formaldehyde adsorption. Srisuad and Virote [21] also reported improved formaldehyde adsorption performance of mesoporous materials obtained by the introduction of amine groups. They argued that the interaction between formaldehyde and ammonia contributed to the increased adsorptivity. Therefore, the improved formaldehyde adsorption performance observed in the present study was attributed to the increase in nitrogen functional groups resulting from an ammonia treatment. The increase in specific surface area due to the formation of micropores might also have contributed to the increased adsorptivity.

**Conclusions**

CMK-3 with a uniform pore structure, large specific surface area, large pore size, and large pore volume was applied to the adsorption of formaldehyde. CMK-H$_2$SO$_4$ and CMK-NH$_3$ were also obtained by a treatment with sulfuric acid and ammonia, respectively. CMK-3 and CMK-3-H$_2$SO$_4$ had a 2D-hexagonal structure, whereas CMK-3-NH$_3$ showed a somewhat disordered structure due to partial destruction of the ordered mesostructure. On the other hand, CMK-3-NH$_3$ had the largest specific surface area and pore volume. XPS showed that only CMK-3-NH$_3$ had nitrogen functional groups, whereas CMK-3-H$_2$SO$_4$ had the largest amount of oxygen functional groups. The order of the adsorption performance against formaldehyde was CMK-3-NH$_3$ > CMK-3-H$_2$SO$_4$ > CMK-3. This was attributed to the combined effects of nitrogen and oxygen functional groups and the specific surface area.

**Abbreviations**

XRD: X-ray diffraction; XPS: X-ray photoelectron spectroscopy.

**Authors’ contributions**

HBA, MJY, JMK, MJ, SSK participated in some of the studies and in drafting the manuscript. YKP conceived of the study and participated in all experiments of this study. Also, YKP prepared and approved the final manuscript. All authors read and approved the final manuscript.

**Competing interests**

The authors declare that they have no competing interests.

Received: 28 September 2011 Accepted: 5 January 2012 Published: 5 January 2012

**References**

1. Kim SS, Kang DH, Choi DH, Yeo MS, Kim KW: Comparison of strategies to improve indoor air quality at the pre-occupancy stage in new apartment buildings. Build Environ 2008, 43:320-328.
2. Jeffrey PO, Lim SF: Airborne concentrations of bacteria in a hospital environment in Singapore. Water Air Soil Pollut 2003, 144:333-341.
3. Thoen A: The sick building syndrome: a diagnostic dilemma. Soc Sci Med 1998, 47:1307-1312.
4. Agents Classified by the IARC Monographs. [http://monographs.iarc.fr/ENG/Classif/index.php](http://monographs.iarc.fr/ENG/Classif/index.php).
5. Wen Q, Li C, Cai Z, Zhang W, Gao H, Chen L, Zeng G, Shu X, Zhao Y: Study on activated carbon derived from sewage sludge for adsorption of gaseous formaldehyde. Bioresour Technol 2011, 102:947-947.
6. Lim JK, Lee SW, Kamin SK, Lee DW, Lee MG: Adsorption characteristics of toluene vapor in fixed-bed activated carbon column. J Environ Sci 2005, 14:61-69.
7. Shin SK, Kang JH, Song JH: Removals of formaldehyde by silver nano particles attached on the surface of activated carbon. J Korean Soc Environ Eng 2010, 32:963-941.
8. Ryu R, Joo SH, Jun SI, Phys J: Synthesis of highly ordered carbon molecular sieves via template-mediated structural transformation. J Phys Chem B 1999, 103:7743-7746.
9. Jun S, Joo SH, Ryu R, Kuk M, Jaroniec M, Liu Z, Ohsuna T, Terasaki O: Synthesis of new, nanoporous carbon with hexagonally ordered mesostructure. J Am Chem Soc 2000, 122:10712-10713.
10. Kang M, Yi SH, Lee HJ, Yie JE, Kim JM: Reversible replication between ordered mesoporous silica and mesoporous carbon. Chem Commun 2002, 1944-1945.
11. Fuentes AB, Neviskaia DM: Control of mesoporous structure of carbons synthesised using a mesostructured silica as template. Micropor Mesopor Mater 2003, 62:177-190.
12. Ryu R, Jum SA: Recent progress on ordered mesoporous carbon molecular sieves synthesized using templated synthesis method. J Korean Ind Eng Chem 2001, 12:1-4.
13. Corma A: From microporous to mesoporous molecular sieve materials and their use in catalysis. Chem Rev 1997, 97:2373-2420.
14. Ciesla U, Schuth F: Ordered mesoporous materials. Micropor Mesopor Mater 1999, 27:131-149.
15. Ying JY, Mehnert CP, Wong MS: Synthesis and applications of supramolecular-templated mesoporous materials. Angew Chem Int Ed 1999, 38:56-77.
16. Davis ME: Ordered porous materials for emerging applications. Nature 2002, 417:813-821.
17. Kim DI, Park JH, Kim SD, Lee JY, Yim JH, Jeon JK, Park SH, Park YK: Comparison of removal ability of indoor formaldehyde over different materials functionalized with various amine groups. J Ind Eng Chem 2011, 17:1-5.
18. Darmstadt H, Roy C, Kaliaguine S, Choi SJ, Ryoo R: Surface chemistry of ordered mesoporous carbons. Carbon 2002, 40:2673-2683.
19. Xia Y, Mokaya R: Synthesis of ordered mesoporous carbon and nitrogen-doped carbon materials with graphitic pore walls via a simple chemical vapor deposition method. Adv Mater 2004, 16:1553-1558.
20. Lee JY, Park SH, Jeon JK, Yoo KS, Kim SS, Park YK: The removal of low concentration formaldehyde over sewage sludge char treated using various methods. Korean J Chem Eng 2011, 28:1556-1560.
21. Srisuda S, Virote B: Adsorption of formaldehyde vapor by amine-functionalized mesoporous silica materials. J Environ Sci 2008, 20:379-384.

doi:10.1186/1556-276X-7-7
Cite this article as: An et al.: Indoor formaldehyde removal over CMK-3. Nanoscale Research Letters 2012, 7:7.