Removal of Indoor Formaldehyde Using Mesoporous Carbon Activated with KOH

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In this study, a mesoporous carbon (CMK-3) activated using KOH was applied to the adsorption of formaldehyde, a representative indoor air pollutant. Activation process was carried out by putting KOH-treated CMK-3 in a reactor maintained at 700 °C in N2 atmosphere. The activated sample was characterized using BET, XRD, XPS and FT-IR analysis. The formaldehyde adsorption performance of the mesoporous carbon was improved, which is attributed to the formation of oxygen and nitrogen functional groups on the mesoporous carbon surface by the activation process.

Keywords: formaldehyde, CMK-3, KOH, adsorption

1. Introduction

Indoor air pollution in a new house is usually caused by volatile organic compounds (VOCs) emitted from building materials and home appliances[1]. Aldehydes are representative indoor-air-polluting VOCs emitted mainly from building materials and tobacco smoke[2]. In particular, formaldehyde (HCHO) has been recognized as a toxic VOC that can cause allergy and severe diseases. Modern people spend more than 80% of their daily lives indoors and their health is threatened significantly by indoor air pollution. Increased air-tightness in buildings aimed at energy saving makes the congestion of indoor air and accumulation of pollutants even more serious[3].

As public interest in environmental pollution increases and the regulation on working environment becomes stricter, the need for efficient recovery of VOCs is increasing, leading to continuous efforts for developing relevant processes and facilities. Adsorption, scrubbing and advanced oxidation have been widely used for treatment of VOCs such as formaldehyde, among which adsorption is the most widely used one[4]. Lee et al.[5] investigated adsorption-desorption characteristics of methyl ethyl ketone (MEK). Shin et al. reported application of silver nanoparticles for removing indoor formaldehyde[3].

The ordered mesoporous carbon materials, recently developed by using mesoporous silica as the mold, have been widely used as adsorbent and support due to its high chemical stability and large BET surface area[6]. Mesoporous carbon materials are also used for other various purposes, e.g., as nano-material support and sensor. Among them, synthesis of silica-templated mesoporous carbons such as CMK-3 has received particularly large attention[7-10]. By filling the pores of mesoporous silica material with carbon material, carrying out pyrolysis, and removing the silica matrix, one can synthesize an ordered mesoporous carbon material. In particular, CMK-3, among others, is a useful material used not only as adsorbent but also as catalyst support because it is easy to synthesize and the mold material SBA-15 is cheap[11]. We have recently applied CMK-3 to adsorption of formaldehyde[12]. However, activation of CMK-3 using KOH for the purpose of formaldehyde adsorption has never been reported.

In this study, removal of formaldehyde using KOH-treated CMK-3 was investigated. The relation between the adsorbent properties and the
adsorption performance was analyzed.

2. Experimental

2.1. Synthesis and Activation of Mesoporous Carbon

SBA-15 (2-d hexagonal) was used as the mold material. Sucrose and sulfuric acid were used as the carbon precursor and the acid catalyst, respectively. For detailed synthesis procedure, one can refer to the literature.[13]

The mesoporous carbon CMK-3 synthesized from SBA-15 was treated with KOH to upgrade its property. After dissolving KOH in distilled water, the solution was mixed with CMK-3 with the KOH/char mass ratio of 1. The mixture was dried for 2 h on a hot plate to evaporate moisture and was then dried again for 24 h in an oven maintained at 110 °C. The reactor was cleaned with N2 gas with the flow rate of 50 mL/min. The dried sample was pulverized before being introduced into the reactor. The reactor was heated up to 700 °C and maintained at that temperature for 1 h. The sample taken out of the reactor was neutralized with 5-M HCl solution, washed with distilled water, and dried for 24 h in an oven maintained at 110 °C. The mesoporous carbon treated this way will be referred to as CMK-3-KOH hereafter.

2.2. Characterization of Mesoporous Carbon

The crystal structure of the synthesized mesoporous carbon powder was analyzed by X-ray Diffraction (XRD, Rigaku D/MAX-III) using a Cu light source (Kα radiation = 1.541 Å).

Pore volume, pore size, and specific surface area of the activated and non-activated mesoporous material samples were measured. TriStar (Micromeritics) was used at -196 °C to obtain the nitrogen adsorption-desorption isotherms for pretreated samples, from which the specific surface area and total pore volume were calculated using the Brunauer-Emmett-Teller (BET) method. The pore size distribution was obtained by the Barrett-Joyner-Halenda (BJH) method.

X-ray Photoelectron Spectroscopy (XPS) measurement was carried out using AXIS-NOVA (Kratos, Inc) to analyze the elements existing on the material surface by measuring kinetic energy distribution of emitted electrons.

FT-IR was used to analyze chemical functional groups existing on the sample surface. The FT-IR measurement was conducted from 550 to 4000 cm⁻¹ to identify oxygen (-COOH, -OH, -COO, -C=O, etc.) and nitrogen functional groups.

2.3. Adsorption of Formaldehyde on Mesoporous Carbon

Adsorption experiments were carried out using 100 ppm formaldehyde gas at 30 °C. Detailed description of the experimental procedure can be found in the literature[14]. The formaldehyde concentration was measured using a formaldehyde analyzer (4000 Series, Woori System, Korea) at 0, 10, 40, and 80 min.

3. Results and Discussion

3.1. Characterization of Mesoporous Carbon

The physical properties of the mesoporous carbon were summarized in Table 1. As is shown in this table, the specific surface area of CMK-3 was 1178 m²/g. CMK-3-KOH had a slightly decreased but still high specific surface area (1130 m²/g). While CMK-3 had pores with their average diameter of 3.8 nm, CMK-3-KOH had significantly
increased micropores due to partial destruction of mesopores by KOH treatment at high-temperature (700 °C). Figure 1 shows the nitrogen adsorption-desorption isotherms and the pore size distributions of the mesoporous carbons. The nitrogen adsorption-desorption isotherms of CMK-3 and CMK-3-KOH are compared in Figure 1(a). Both samples exhibited type IV isotherms, which are typical for mesoporous materials, with a leap at relative pressure (P/P₀) of 0.5.

The surface elemental compositions of the mesoporous carbons analyzed by XPS are shown in Table 2. Compared to CMK-3, CMK-3-KOH had less carbon and more oxygen. Nitrogen was also observed on the surface of CMK-3-KOH, which was not the case for CMK-3. This result can be attributed to the formation of oxygen and nitrogen functional groups on the surface of CMK-3 during the activation process, which may enhance the adsorption performance. It is presumed that the formation of oxygen functional groups stemmed from KOH treatment, whereas the nitrogen functional groups were formed by high-temperature treatment.

XRD analysis was performed to investigate the effect of activation on the crystal structure of the mesoporous adsorbents. Figure 2 compares the XRD patterns of CMK-3 and CMK-3-KOH. From the low-
angle and high-angle patterns of XRD, it was shown that the mesostructure of CMK-3 had a 2D-hexagonal XRD pattern. In the meantime, the low-angle pattern of CMK-3-KOH (2(a)) showed that the mesopore structure of CMK-3-KOH was destructed, which is attributed to the rapid KOH treatment at high-temperature (700 °C).

Figure 3 shows the O1s and N1s spectra of mesoporous carbons obtained by XPS analysis. In the O1s spectra (3(a), 3(b)), the largest peak was generally observed at the binding energy level of 532.8 eV (±0.5 eV), which is C=O peak[15], although the peak intensity was changed by activation. Both CMK-3 and CMK-3-KOH showed four peaks. The peaks observed at the binding energy levels of 531.1 eV (±0.5 eV), 535.1 eV (±0.5 eV), and 537.6 eV (±0.5 eV) are C-OH, O3 and O4 peaks, respectively[15]. Figure 3(c) shows the N1s spectrum of CMK-3-KOH. Two peaks were observed in the N1s spectrum at the binding energy levels of 399.2 eV (±0.5 eV) and 400.9 eV (±0.5 eV), which represent nitrogen atom and pyridine-like nitrogen, respectively[16].

Figure 4 shows the FT-IR spectra from which the functional groups formed on the activated mesoporous carbon surface can be identified. As was reported in the literature[17,18], the intensity of the C=O or C=N peak appearing at 1700∼1800 cm⁻¹ was increased by KOH treatment. It is also shown that the intensities of the C-O peak appearing at 1200∼1300 cm⁻¹ and the nitro group peak or C=O peak appearing at 1300∼1400 cm⁻¹ were increased by KOH treatment.

3.2. Adsorption of Formaldehyde on Mesoporous Carbons

Figure 5 shows the experimental results of formaldehyde adsorption on CMK-3 and CMK-3-KOH. Adsorption occurred most rapidly for the first 10 min. CMK-3 showed a high adsorption efficiency of about 50% resulting from its high specific surface area (1178 m²/g). CMK-3-KOH exhibited even better adsorption performance than CMK-3 despite its slightly smaller specific surface area (1130 m²/g), which can be ascribed to increased oxygen and nitrogen functional groups indicated by surface composition, XPS and FT-IR analyses. In particular, the surface composition analysis showed that CMK-3-KOH had a larger amount of oxygen functional groups (8.33%) than CMK-3 (2.11%) and also had nitrogen functional groups that were not observed on the surface of CMK-3. The higher adsorption efficiency of CMK-3-KOH than that of CMK-3 is in good agreement with the result shown in Figure 4; the peak intensities of CMK-3-KOH at the wave numbers 1200∼1300 cm⁻¹, 1300∼1400 cm⁻¹, and 1700∼1800 cm⁻¹ decreased to a larger extent as a result of adsorption than those of CMK-3.

4. Conclusions

In this study, mesoporous carbon, one of the ordered mesoporous materials that have been widely used as adsorbent and catalyst support due to their high chemical stability and large BET surface area, was applied to adsorption of formaldehyde after activation using KOH. The activation improved the formaldehyde adsorption performance in spite of a slight reduction of the specific surface area. XRD analysis result indicated that the mesoporous carbon structure was destructed after KOH treatment. XPS analysis showed that oxygen and nitrogen functional groups were formed by the activation process. From the FT-IR spectra, it was shown that CMK-3-KOH had higher peak intensities for the oxygen and nitrogen peaks than CMK-3 and that the decrease in the peak intensity due to adsorption was larger for CMK-3-KOH than for CMK-3. It is believed that the formation of oxygen and nitrogen groups on the mesoporous carbon surface by activation led to improved adsorption performance despite the destruction of mesoporous carbon structure.

References