



Influence of surface functionalities on ethanol adsorption characteristics in activated carbons for adsorption heat pumps



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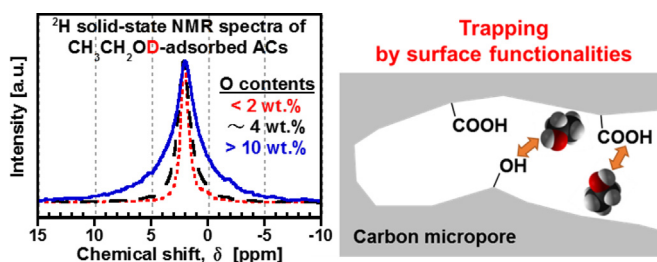
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HIGHLIGHTS

- Activated carbons with different oxygen contents but similar porosity were prepared.
- Abundant surface functionalities caused a lowering of ethanol adsorption amounts.
- Abundant surface functionalities caused a shortening of adsorption equilibrium times.
- Surface functionalities induced a diffusional hindrance of ethanol in micropores.
- NMR and electrochemical analyses supported the findings in adsorption measurements.

GRAPHICAL ABSTRACT



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ABSTRACT

To develop high-performance activated carbons (ACs) for adsorption heat pumps (AHPs), it is important to characterize the adsorption behaviors of the refrigerant molecules in the pores of ACs. Not only pore structures, such as pore size and shape, but also surface functionalities strongly influence the adsorption behaviors, especially for polar molecules, such as water and ethanol, which are typical refrigerants for AHP. In this study, we examined the influence of surface functional groups on the adsorption behaviors of ethanol molecules in carbon micropores using model ACs with different amounts of oxygen-containing surface functional groups but comparable porosities. For the AC with an increased amount of surface functional groups, ethanol adsorption/desorption isotherms showed significant decreases in the adsorption amounts and shortened adsorption equilibrium times compared to those with less surface functional groups throughout the entire relative pressure region. This suggests diffusional hindrance of ethanol molecules in micropores with abundant surface functional groups. To verify our hypothesis, we examined the influence of surface functional groups on the adsorption behavior of ethanol molecules using a solid-state NMR technique. The NMR results revealed that the hydroxyl group of ethanol molecules strongly interacts with the surface functional groups, giving rise to an oriented adsorption of

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ethanol molecules in the micropores with oxygen-containing surface functional groups. Furthermore, electrochemical analyses confirmed that diffusion resistance of electrolyte ions in the micropores increases after the introduction of oxygen-containing surface functional groups, which supports our hypothesis.

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1. Introduction

Heat pumps are an environmentally friendly system that provides heating and cooling effects using relatively low-level heat sources such as solar energy, geothermal heat, and industrial waste heat [1,2]. Recently, adsorption heat pumps (AHPs) have been actively studied and developed because they can effectively use low-temperature waste heat at around 373 K or lower. Two approaches have been used to improve the performance of AHP systems: chemical engineering-based and material-based approaches. For the latter approach, various adsorbent–adsorbate pairs, such as silica gel–water [3,4], zeolite–water [5], activated carbon (AC)–CO₂ [6], AC–water [7], AC–methanol [8,9], and AC–ethanol [1,9] pairs, have been considered because adsorptive and thermal characteristics depend not only on individual properties of the adsorbent and adsorbate, but also on their combination. Demir et al. [10] discussed problems and solutions associated with AHP systems. For example, the zeolite–water pair showed low adsorbability of approximately 30 wt.% of the adsorbent. On the other hand, the AC–ethanol pair showed much higher adsorption properties of more than 150 wt.% of the adsorbent [11]. Attan et al. [12] also reported that AC fiber, which has a high specific surface area, high total pore volume, and narrow average pore size, showed good adsorptivity for numerous refrigerants, including water, ammonia, acetone, methanol, and ethanol. However, the adsorption behavior is influenced not only by pore structures, but also by surface functionalities, especially for polar molecules such as water and ethanol. In this study, we explored the role of surface functionalities of ACs on the adsorption behavior of ethanol molecules in carbon micropores.

To examine the influence of surface functionalities, model AC samples with comparable pore structures but different quantities of surface functionalities were required. Therefore, we controlled the oxygen contents using heat treatments in H₂ or with KOH while maintaining the pore structure using an ultrahigh-surface-area AC, Maxsorb III [13], as the parent material. The model AC samples were used to investigate the influence of surface functionalities on adsorption performance, such as adsorption amounts and kinetics, as well as the adsorption states of the ethanol molecules in carbon micropores using solid-state nuclear magnetic resonance (NMR). NMR spectroscopy is based on physical phenomena of nuclei in a magnetic field absorbing and re-emitting electromagnetic radiation; NMR can provide detailed information regarding the structure, dynamics, and chemical state of molecules and is a powerful method for analyzing adsorption states of molecules and ions [14]. Moreover, electrochemical techniques, *i.e.*, cyclic voltammetry and electrochemical impedance spectroscopy, were applied to obtain diffusional information on the materials (electrolyte ions) in carbon micropores with different amounts of oxygen-containing surface functional groups. Based on these results, we examined the influence of surface functionalities on the adsorption behaviors of molecules in the carbon micropores.

2. Experimental

Three AC samples were used in this study: Maxsorb III from Kansai Coke and Chemicals Co., Ltd. (designated as MAX in this

study), H₂-treated Maxsorb III (with lower contents of oxygen-containing functional groups, named H-MAX), and KOH-activated H₂-treated Maxsorb III (with higher contents of oxygen-containing functional groups, abbreviated as Ox-MAX). H-MAX was prepared using heat treatment of MAX under a reducing atmosphere (Ar/H₂ = 8/2 (v/v), total flow rate = 250 cm³/min) at 600 °C for 24 h. To prepare Ox-MAX, KOH treatment was applied to H-MAX at a KOH/carbon weight ratio of 2. The mixture was heat-treated at 600 °C for 1 h under N₂ flow (100 cm³/min). After the reaction, the remaining KOH and salts that formed during the heat treatment were removed by washing with HCl solution three times and deionized water once to adjust the pH to approximately 7. After washing, the collected samples were dried at 100 °C for 3 h in an air oven and dried again at 150 °C for 3 h in a vacuum oven.

Elemental compositions of AC samples were analyzed using a CHN analyzer (MT-5, Yanako, Japan). The assay of O content (O_{diff.}) was defined by subtracting the sum of the contents of C, H, and N from 100%. N₂ adsorption/desorption isotherms at 77 K were measured using volumetric adsorption equipment (Belsorp-Max-S, BEL Japan Inc., Japan) to investigate porosity. Ethanol adsorption/desorption kinetics and isotherms were gravimetrically measured at 303 K. Fig. 1 shows the schematic diagram of a gravimetric adsorption apparatus. A sample was placed in a sample basket and into an adsorption chamber. Prior to adsorption measurements, the sample was pretreated at 150 °C under vacuum for 2 h. After cooling the sample, isothermal water and air baths were set to

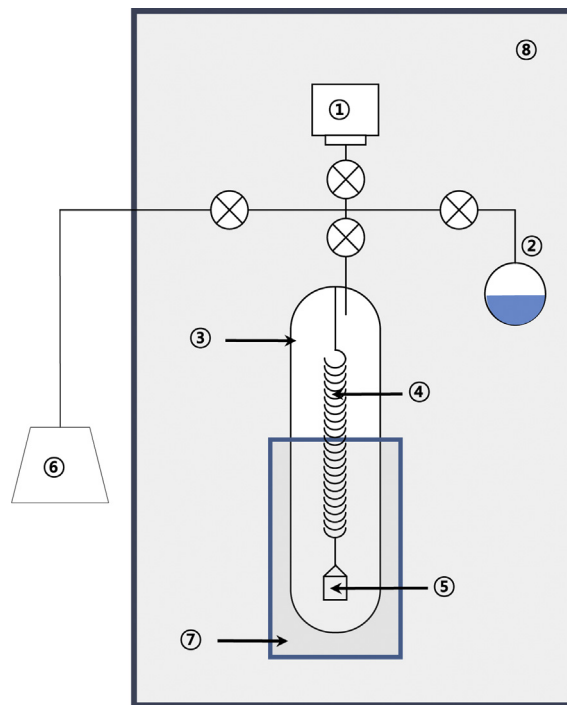


Fig. 1. Schematic diagram of the gravimetric adsorption apparatus. 1. Pressure gauge, 2. Liquid ethanol vessel, 3. Adsorption chamber, 4. Quartz spring, 5. Sample basket, 6. Diffusion and rotary pumps, 7. Isothermal water bath, 8. Isothermal air bath.

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