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Inhibition of nitrobenzene adsorption by water cluster formation at acidic oxygen functional groups on activated carbon

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ABSTRACT

The inhibition effect of nitrobenzene adsorption by water clusters formed at the acidic groups on activated carbon was examined in aqueous and *n*-hexane solution. The activated carbon was oxidized with nitric acid to introduce C–O complexes and then outgassed in helium flow at 1273 K to remove them completely without changing the structural properties of the carbon as a reference adsorbent. The amounts of acidic functional groups were determined by applying Boehm titration. A relative humidity of 95% was used to adsorb water onto the carbon surface. Strong adsorption of water onto the oxidized carbon can be observed by thermogravimetric analysis. The adsorption kinetic rate was estimated to be controlled by diffusion from the kinetic analysis. Significant decline in both capacity and kinetic rate for nitrobenzene adsorption onto the oxidized carbon was also observed in *n*-hexane solution by preadsorption of water to the carbon surface, whereas it was not detected for the outgassed carbons. These results might reveal that water molecules forming clusters at the C–O complexes inhibited the entrance of nitrobenzene into the interparticles of the carbon.

1. Introduction

Adsorption plays an important role in removing contaminated organic compounds from gaseous and liquid fluids in numerous regions in industries. Activated carbons are typical porous adsorbents utilized for treatment of exhausted gas, solvent recovery, and various water treatments [1,2]. The adsorption ability is generally dependent on surface area, pore size distribution, and surface nature. In particular, acidic functional groups such as carboxylic and lactonic groups significantly affect adsorption performance even though they are present in small amounts on the surfaces of activated carbons [3]. For aromatics adsorption onto activated carbons in aqueous solutions, the more surface acidic groups there are, the more the adsorption capacity is decreased [4–6]. The hydrophilic acidic carboxyl and lactonic groups at the edge of the graphene layer could strongly attract water molecules, leading to the formation of water clusters. After this, the adsorbates in the solution are estimated to be hindered from entering inside the pores [7,8]. Pinto and co-workers examined adsorption in nonpolar solvents instead of the polar solvent water to prevent the pores from being blocked by the formation of water clusters [8–10]. In our previous study, the increase in adsorption of phenol and nitrobenzene was observed with increased acidic functional groups in *n*-hexane solution, whereas the opposite results were obtained in aqueous solutions [11]. In the aqueous phase, pH significantly affects the surface charge of the carbon surface and the chemical species of solutes, affecting the adsorption capacity [12,13]. In addition, the liquid phase adsorption is also influenced by solubility of the adsorbate in the solvent and affinity between the adsorbate and the adsorbent surface, making the adsorption mechanism complicated [14,15]. Although changes in adsorption amounts have been repeatedly observed by altering the amount of surface functional groups by oxidation and outgassing [16–18], the mechanism for the decrease in aromatics adsorption on oxidized carbon has not been clearly elucidated yet. The formation of water clusters at the inlets of pores has been proposed [8], which may be supported only by a molecular simulation study by Müller and Gubbins [19]. In this study, the inhibition effect of aromatics adsorption was examined by measurements of adsorption capacities and kinetics using oxidized activated carbons possessing acidic functional groups with and without water vapor preadsorption onto the surface, compared with outgassed counterparts in which no acidic functional groups resided. Desorption profiles of preadsorbed water for the oxidized and the outgassed carbons were also inspected at elevated temperature by a thermogravimetric analysis.

2. Experimental

2.1. Activated carbons

Commercially available petroleum-pitch-based activated carbon (AC) of bead shape, purchased from Kureha Corporation, Japan, was

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employed for the experiments. The AC was boiled in de-ionized water to thoroughly remove contaminated fine powder. The oxidation to introduce acidic groups onto the carbon surface was conducted according to the procedure of Radovic et al., described as follows [20]. The AC was put into 7.5 mol/L nitric acid, heated to 363 K, and maintained for 6 h, then cooled to room temperature and repeatedly rinsed with de-ionized water, and finally heated in air at 623 K for 4 h to decompose the nitrate ions still remaining after the water washing; the oxidized activated carbon is referred to as Ox-AC. Furthermore, outgassing was carried out to prepare reference materials; the Ox-AC was placed in a quartz tube and heated to 1273 K in 99.9995+% purity helium flow, and the temperature was kept for 30 min to eliminate surface acidic groups as CO, CO_2, and H_2O; the resulting material was denoted as OxOG-AC.

2.2. Determination of acidic groups

Boehm titration was applied to quantitatively determine the acidic and basic surface functional groups/sites on the prepared ACs [21]. Six hundred milligrams of the prepared AC and 15 mL of $NaHCO_3$ (0.1 mol/L), Na_2CO_3 (0.05 mol/L), or NaOH (0.1 mol/L) solution was mixed in a conical flask and agitated at 100 rpm for 4 days at 298 K, and then a 5 mL aliquot of the solution for each sample was back-titrated with HCl (0.1 mol/L). The $NaHCO_3$ neutralizes only carboxylic groups on the carbon surface, Na_2CO_3 neutralizes carboxylic and lactonic groups, and NaOH reacts with carboxylic, lactonic, and hydroxyl groups. Accordingly, the difference between the groups neutralized by $NaHCO_3$ and Na_2CO_3 becomes lactones; the difference between those neutralized by Na_2CO_3 and NaOH is hydroxyls. The same procedure was carried out for a mixture of 0.6 g of the carbons and 15 mL of HCl (0.1 mol/L) solution to determine the basic sites of the carbon surface. After an excess amount of NaOH (0.1 mol/L) solution was added to the remaining HCl solution, the NaOH solution was titrated with HCl (0.1 mol/L) solution again. Neutralization points were detected using methyl red solution indicator for a weak base titrated with strong acid, and phenolphthalein solution for a strong acid and strong base combination.

2.3. Surface area of activated carbon

Specific surface area and pore distribution were measured by Backman Coulter Model SA-3100. From the adsorption–desorption isotherms of nitrogen gas at 77 K, specific surface area and micropore surface area (<2 nm) were calculated by BET and *t*-plot methods, respectively. Meso- and macropore area was determined by subtracting micropore surface area from BET surface area.

2.4. Water vapor adsorption

Relative humidity (RH) inside the desiccator was adjusted to 95% using a saturated aqueous solution with KNO_3 [22]. The desiccator, including the weighed dried ACs and hydrometer, was placed in the thermostatic chamber and kept for 12 h to absorb moisture to establish equilibrium, denoted as Ox-RH95 and OxOG-RH95 for Ox-AC and OxOG-AC, respectively.

2.5. Thermogravimetric analysis

Decrease in weight at elevated temperature in nitrogen flow was detected using a Seiko Instruments TG/DTA Model EXSTAR6000. The moisture-adsorbed AC was accurately weighed to about 10 mg, put into a small cylindrical aluminum container, and placed on a platinum plate attached to the TG/DTA weighing system. The weight loss, assumed equal to the amount of water desorption, were observed at increasing temperature from ambient up to 373 K at a speed of 2 K/min.

Table 1
Structural and surface properties of activated carbons

	AC	Ox-AC	OxOG-AC
BET surface area (m^2/g)	1300	820	800
Micro-pore surface area (m^2/g)	1160	290	300
Meso- and macro-pore surface area (m^2/g)	140	530	500
Surface functional groups (mmol/g)			
Carboxylic groups	0.00	0.91	0.00
Lactonic groups	0.00	0.22	0.00
Phenolic groups	0.14	1.35	0.18
Total acidic groups	0.14	2.48	0.18
Total basic groups/sites	0.48	0.14	0.48

2.6. Adsorption

Chemicals used for adsorption experiments were commercially purchased in reagent grade. Fifty mg of activated carbon was dosed into 25 mL of de-ionized water or *n*-hexane solution of nitrobenzene in a 100-mL conical flask and agitated at 100 rpm at 298 K. The initial concentration of nitrobenzene ranged from 0.46 9.7 mmol/L for adsorption isotherms and was adjusted to 1.6 mmol/L for kinetic rate measurement. At least 48 h was taken as the agitation time to obtain the adsorption isotherms, because in our preliminary study it was a sufficient period to establish equilibrium for both aqueous and *n*-hexane solution. The amount of adsorption onto the activated carbon was calculated from the difference in concentration between the initial and the final solution. The nitrobenzene concentration in the solution was determined using UV absorption at 260 nm with a Shimadzu UV-2550 spectrometer. The aqueous solution pH in the aqueous solution was measured by a portable pH meter (HORIBA Model D-51).

3. Results and discussion

3.1. Properties of activated carbons

Textural and surface characteristics of the activated carbons are tabulated in Table 1. A 40% decline in specific BET surface area and an increase in meso- and macropore and a decrease in micropore surface area were observed for the AC oxidized by the nitric acid, revealing that the oxidation collapsed the structure, converting micropore to meso- and macropore structures [23]. The surface nature was also greatly changed by the oxidation, introducing carboxylic, lactonic, and phenolic groups onto the AC, referred to as Ox-AC. These acidic C–O complexes are assumed to become strong water adsorption sites. The outgassing of oxidized AC, denoted OxOG-AC, represents complete removal of carboxylic and lactonic groups from the AC surface, but no significant change can be detected in structure and total surface area, as can be seen in Table 1. Comparing Ox-AC with OxOG-AC, carbons of the same surface area and pore distribution but different surface chemistry could be prepared by sequential treatments of oxidation and outgassing [24].

3.2. Water vapor adsorption

Fig. 1 provides water vapor adsorption kinetics at 298 K at relative humidity (RH) 95% for Ox-AC and OxOG-AC. It took more than 4 h to reach the adsorption equilibrium, and gave similar adsorption amounts of about 0.3 g per gram of activated carbon. The extent of water adsorption may be greater for Ox-AC than for OxOG-AC in the lower humidity, because the acidic groups become strongly attractive sites toward water vapor. However, at humidity as high as 95% in this experiment, capillary condensation and continuous pore filling can play a predominant role in water vapor adsorption; the water adsorption is dependent on the structure