

Effect of Surface Oxidation of Active Carbon on Ammonia Adsorption

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The behavior of ammonia adsorption was studied on various types of surface-treated active carbon (HNO_3-AC, H_2SO_4-AC, HCl-AC, NaOH-AC, CuO-AC, and H_2-AC) under 0–75 kPa and 323–473 K. Amount of ammonia adsorption on active carbon was increased by the surface oxidation through acid treatment or metal nitrate decomposition. It was decreased by the hydrogen treatment at 1173 K. The equilibrium amount of ammonia adsorption was found to relate with the amount of surface organic oxygen. Ammonia adsorption was analyzed through the isotherm and classified into three types: (1) strong adsorption relating to surface organic oxygen content and being independent of pressure, (2) weak adsorption relating to surface organic oxygen content and depending upon the pressure, (3) van der Waals adsorption. The model well represented the data, and the average relative error was 10%. When the samples are assumed to be used for ammonia separation with temperature swing adsorption method (323–473 K, 40 kPa), H_2SO_4-treated active carbon was found to have the highest ammonia separation capacity (2.58 mmol g^{-1}).

At the NO_x emission sites such as power plants and disposal furnaces, liquid ammonia is used as a reducing agent for NO_x removal. Liquid ammonia used for this purpose is costly because of the transfer and the storage due to its toxicity. If ammonia can be produced on-site efficiently, the transfer and storage are made unnecessary. A new de-NO_x process with ammonia on-site synthesis has been proposed by our group as an answer of this problem.[1] Here, development of an ammonia adsorbent such as active carbon for separation and storage at 40–80 kPa of ammonia synthesized on-site is a key for practical use of the process.[1]

The characteristics of active carbon as adsorbent are high surface area with porous structure and hydrophobic nature. Therefore, active carbon is an effective adsorbent for non-polar or low polar gas such as hydrocarbon and halocarbon, but it is less effective for adsorption of polar gas such as ammonia.[2] Nevertheless the high surface area of active carbon is still attractive; thus, improvements with surface treatment have been attempted. Two kinds of surface treatment methods have been proposed. The first one is acid treatment, which oxidizes the surface carbon atoms turning them to functional groups containing oxygen atom or leaving acids as they are (H_2SO_4, H_3PO_4, et al.).[3–7] Those functional groups or acids can adsorb ammonia through ammonium ion formation. The second is deposition of metal salt or metal oxide. The aim of deposition of these compounds is to increase the ammonia adsorption site due to coordination.[7–10] Several works about ammonia adsorption on active carbon as ammonia reservoir for NO reduction have been reported.[11–13] However, ammonia pressure studied in these works are quite low (such as 0.1 kPa).[3–13] Although the materials are similar, the functions are different under the different conditions.

In a previous paper, sulfuric acid-treated active carbon was proposed as an ammonia adsorbent for the process; however, other treatments for active carbon and adsorption mechanisms have not been studied yet.[1]

In this paper, ammonia adsorption behaviors of six types of surface treated active carbon (HNO_3-AC, H_2SO_4-AC, HCl-AC, H_2-AC, NaOH-AC, and CuO-AC) are studied. The surface treatment effect on ammonia adsorption, the prediction method of ammonia adsorption amount, and the adsorption mechanism shall be discussed. Finally, possibility of these surface treated active carbon as the ammonia separation-storage material for the practical process shall be discussed.

Experimental

Sample Preparation and Characterization. Active carbon pellets (Kanto Kagaku) were used as a standard adsorbent of active carbon (AC). Three kinds of treated AC were prepared with different methods.

1) AC was added to HNO_3, H_2SO_4, or HCl aqueous solution (3 mol L^{-1}), which was stirred at room temperature for 3 h, and was evaporated at 373 K. The acid treated AC sample was dried in air at 383 K for overnight, and calcined in He flow at 773 K for 3 h.
2) AC was impregnated with $NaNO_3$ (99%; Kanto Kagaku) or $Cu(NO_3)_2 \cdot 3H_2O$ (99.9%; Wako Chemicals) in water, and calcined in He flow at 773 K for 3 h to prepare NaOH or CuO and to oxidize AC (NaOH-AC, CuO-AC).
3) H_2-treated AC (H_2-AC) was prepared by treating the carbon in flowing H_2 flow at 1173 K for 90 h.[14–16]

The composition of organic components in these kinds of surface-treated AC was determined by elemental analysis with a combustion method. The inorganic oxygen in metal oxide deposited AC

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was excluded because it was counted as the ash element. The BET surface area of these samples was measured by N_2 adsorption after evacuation at 723 K for 2 h. The N_2 adsorption and desorption isotherms were obtained with an automatic gas adsorption apparatus (BELSORP 28SA; BEL Japan).

Ammonia Adsorption Measurement. The ammonia adsorption isotherms were obtained by volumetric method with a closed system made of Pyrex glass. The pressure after 10 min from ammonia introduction was regarded as the adsorption equilibrium pressure. Each ammonia adsorption isotherm was measured between 0 and 75 kPa at 323 K or 473 K, and the measurements were done two times for each isotherm. The amount of ammonia adsorbed at the first measurement was denoted as the total adsorption. The sample was evacuated to remove (reversibly adsorbed) ammonia at the same temperature for 1 h, then the second (reversible) adsorption was carried out.

Results

Sample Composition of Surface-treated AC. The surface area and the sample composition of organic components in various kinds of surface-treated AC are shown in Table 1. Inorganic components are presented as "others." The previously reported sample (H_2SO_4-AC-w; starting AC was provided from Wako Chemicals) is also shown as reference data.[1] The elemental analysis of H_2SO_4-AC-w was not done. The surface treatment (acid treatment, metal oxide deposition, and H_2 treatment) did not cause extensive surface area reduction. The oxidation of AC by HNO_3 or H_2SO_4 treatment was confirmed by the increase of the ratio of oxygen to carbon.[17–20] However, HCl treatment was not effective for the oxidation of AC. The oxidation of AC by $NaNO_3$ or $Cu(NO_3)_2$ decomposition was also confirmed. On the other hand, surface species of AC was removed by H_2 treatment, which was confirmed by the decrease of oxygen, sulfur, nitrogen, and halogen.[14–17]

Surface Treatment Effect of Active Carbon on Ammonia Adsorption Behavior. Ammonia adsorption measurements were done for active carbon with three kinds of treatments. Here, the amount of ammonia adsorption under standard conditions (40 kPa, 323 and 473 K) on all the samples is summarized in Table 2.[1] The detailed data shall be shown below for each treatment.

The results of ammonia adsorption of various kinds of acid-treated AC (HNO_3-AC, HCl-AC, and H_2SO_4-AC) measured at 323 K are shown in Fig. 1. The amount of ammonia adsorption on HNO_3-AC or H_2SO_4-AC is higher than that on non-treated AC, and increases steeply below 10 kPa (chemisorption) and linearly above 10 kPa (physisorption). Further, there is some irreversible adsorption on those kinds of acid-treated

Table 1. Elemental Analysis of Active Carbon with Various Treatment

Sample	Surface area	C	H	O	N	S	Cl	Others[a]
	$m^2\ g^{-1}$	wt %	wt %	wt %	wt %	wt %	wt %	wt %
Standard								
AC	1161	96.4	0.5	2.1	0.2	0.1	0.3	0.3
Acid treated								
HNO_3-AC	1010	85.7	0.8	11.9	0.8	0.1	0.2	0.5
H_2SO_4-AC	1016	90.6	0.8	7.9	0.2	0.1	0.0	0.4
HCl-AC	1039	95.1	1.1	2.3	0.3	0.1	1.2	0.0
Metal oxide deposited								
NaOH-AC	1125	55.9	0.9	4.3	0.1	0.1	0.5	38.3
CuO-AC	905	73.8	1.4	6.8	1.1	0.4	0.1	16.6
Hydrogen treated								
H_2-AC	1122	97.4	0.6	0.8	0.2	0.0	0.0	1.1
Reference data								
H_2SO_4-AC-w[b]	848							

a) Inorganic component such as metal oxide. b) Previously reported data as reference.[1]

Table 2. Ammonia Adsorption Capacity of Surface Treated Active Carbon at 40 kPa

Sample	323 K[a] Total[b]	Reversible[c]	Irreversible[d]	Rev./Total	473 K[a] Total[b]
	$mmol\ g^{-1}$	$mmol\ g^{-1}$	$mmol\ g^{-1}$		$mmol\ g^{-1}$
AC	1.19	1.15	0.04	0.97	0.14
HNO_3-AC	3.07	2.60	0.47	0.85	0.63
H_2SO_4-AC	2.78	2.45	0.33	0.88	0.20
HCl-AC	1.21	1.16	0.05	0.96	<0.1
NaOH-AC	1.69	1.47	0.22	0.87	0.29
CuO-AC	2.49	2.26	0.23	0.91	0.40
H_2-AC	0.66	0.66	<0.01	1.00	<0.1
H_2SO_4-AC-w[e]	2.45				0.70

a) Adsorption temperature. b) Adsorption amount of 1st measurement. c) Adsorption amount of 2nd measurement. d) Difference between total amount and reversible amount. e) Previously reported data as reference.[1]

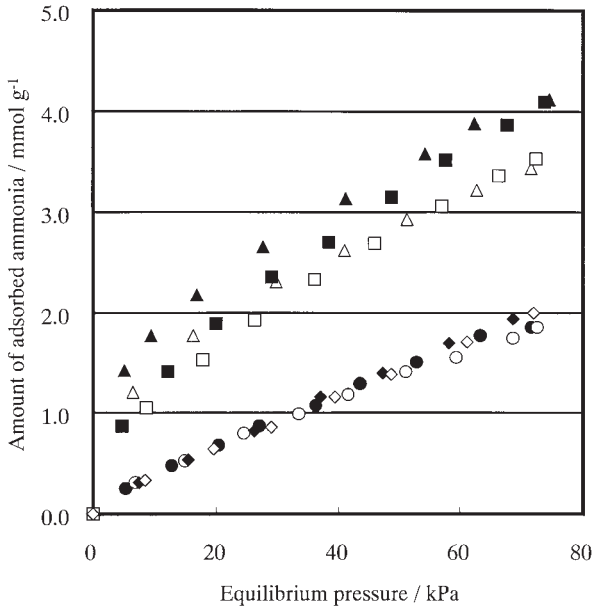

Fig. 1. Adsorption isotherm of ammonia (closed symbol: first measurement; open symbol: second measurement) on acid treated active carbon measured at 323 K; (●, ○) non-treated AC, (▲, △) HNO_3-AC, (■, □) H_2SO_4-AC, (◆, ◇) HCl-AC.

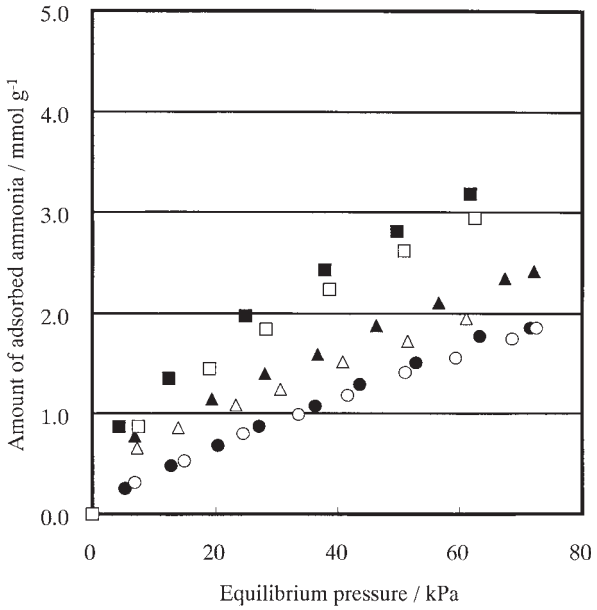

Fig. 2. Adsorption isotherm of ammonia (closed symbol: first measurement; open symbol: second measurement) on metal oxide deposited active carbon measured at 323 K; (●, ○) non-treated AC, (▲, △) NaOH-AC, (■, □) CuO-AC.

AC (Fig. 1 and Table 2). This indicates that HNO_3 or H_2SO_4 treatment produces chemisorption sites for ammonia adsorption. On the other hand, the behavior of ammonia adsorption on HCl-AC was almost the same as that on non-treated AC. The organic oxygen contents of HNO_3-AC and H_2SO_4-AC are higher than that of non-treated AC; however, that of HCl-AC is almost the same as that of non-treated AC (Table 1). The surfaces of HNO_3-AC and H_2SO_4-AC are oxidized[17–20] or form some kind of functional groups (–OH, –COOH, $–SO_3H$, $–NO_2$, and others), which must be related with ammonia adsorption. These are considered to be chemisorption sites due to ammonium ion formation and electrostatic attraction. Any remaining Cl (Table 1) is not effective, probably because Cl ions are occluded between the graphite layer structures and are not exposed on the surface.

The results of ammonia adsorption of metal nitrate-decomposed AC (NaOH-AC and CuO-AC) measured at 323 K are shown in Fig. 2. Amounts of ammonia adsorption on these samples are higher than that on non-treated AC; furthermore there is some irreversible adsorption (difference between the first and the second adsorption). The shape of ammonia adsorption isotherms are similar to those on HNO_3-AC and H_2SO_4-AC. This suggests that NaOH and CuO deposition through nitrate decomposition create new ammonia adsorption sites. Organic oxygen content of NaOH-AC and CuO-AC are high, while ash content is also high due to the resulting metal oxide or hydroxide (Table 1).

Ammonia adsorption isotherm on H_2 treated AC (H_2-AC) measured at 323 K is shown in Fig. 3. The amount of ammonia adsorption is low and increases linearly with the pressure, suggesting the physisorption. Elemental analysis shows that O, S, Cl, and others are decreased by hydrogen treatment at 1173 K (Table 1). The surface functional groups of active

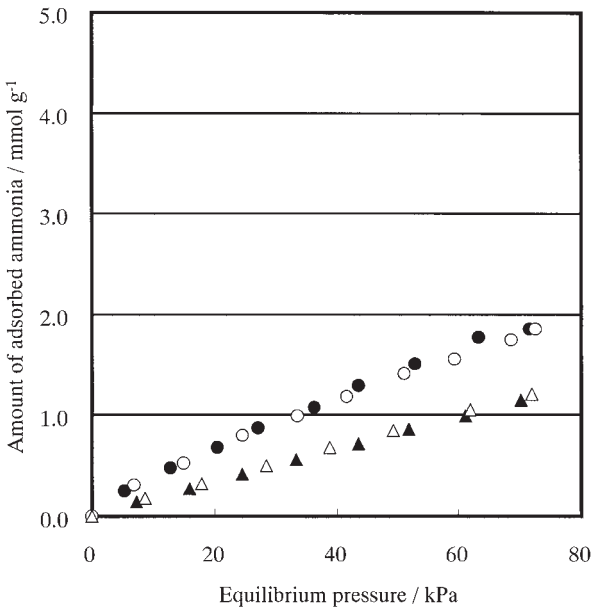

Fig. 3. Adsorption isotherm of ammonia (closed symbol: first measurement; open symbol: second measurement) on hydrogen treated active carbon measured at 323 K; (●, ○) non-treated AC, (▲, △) H_2-AC.

carbon are removed by the hydrogen treatment.[14–17] Such surface functional groups are suggested to be responsible for ammonia adsorption. Ammonia can adsorb on H_2-AC only with van der Waals forces.

Discussion

Evaluation of Ammonia Adsorption at 323 K under 40 kPa as a Function of Organic Oxygen Content. Table 2

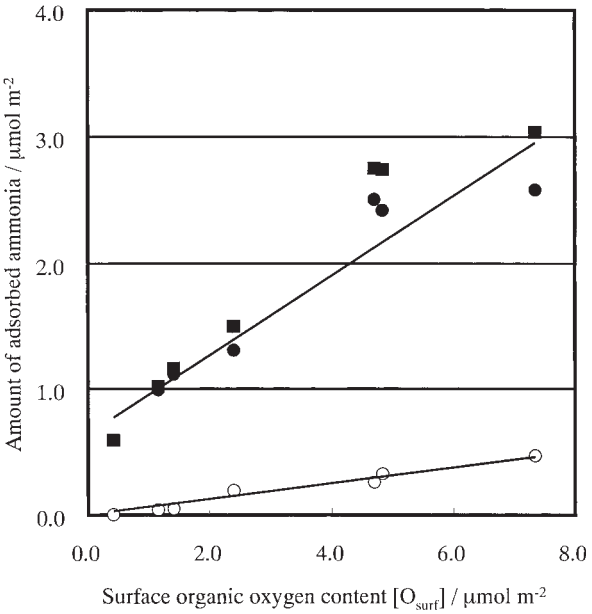

Fig. 4. Surface organic oxygen content dependence on ammonia adsorption amount (under 40 kPa) of various surface treated active carbon; (●) reversible adsorption, (○) irreversible adsorption, (■) total amount.

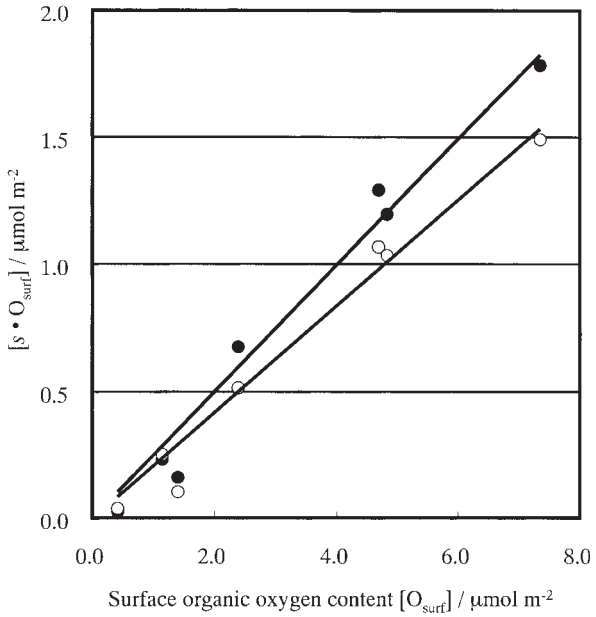

Fig. 5. Surface organic oxygen content dependence on s (intercept extrapolated from ammonia adsorption isotherm above 30 kPa) of various surface treated active carbon; (●) 1st measurement, (○) 2nd measurement.

shows that amounts of reversibly and irreversibly adsorbed ammonia do not depend on the specific surface area of samples. Here, ammonia adsorption amount "under 40 kPa" on various samples is shown as a function of organic oxygen content in Fig. 4.

The amount of reversibly adsorbed ammonia "under 40 kPa" (filled symbols) seem to have the first order relation with surface organic oxygen content with a slope of $NH_3(a)/O_{surf} = 0.31$. Here, $NH_3(a)$ and O_{surf} mean moles of adsorbed ammonia and moles of surface organic oxygen, per surface area respectively. We assume that the oxygen measured by the elemental analysis includes such oxygen which is directly bound on the carbon surface and are not such oxygen as is contained in the ash "compounds." The amount of irreversibly adsorbed ammonia increased linearly with surface organic oxygen content, with a slope of $NH_3(a)/O_{surf} = 0.062$. This suggests that ammonia is irreversibly adsorbed through the strong interaction with surface organic oxygen species (such as ammonium ion formation, hydrogen bond formation, or strong electrostatic attraction). This irreversible adsorption occurs at quite low pressure. The amount of irreversibly adsorbed ammonia at 473 K (not listed) was much lower than that at 323 K (Table 2). The irreversibly adsorbed ammonia defined here does not desorb through evacuation, but does desorb through heating.

Evaluation of Ammonia Adsorption as Functions of Pressure and Surface Organic Oxygen Content. The amount of reversibly adsorbed ammonia is not zero on the sample free from organic oxygen because of the interaction between ammonia and the surface. Now the ammonia adsorption isotherm was analyzed through both organic oxygen content and ammonia pressure.

Here, three types of interaction between ammonia and the sample surface are assumed. The first type (strong interaction) occurs prior to any other type at quite low pressure, and it depends on only organic oxygen content. The second type (weak interaction) occurs through the surface organic oxygen, but depends on ammonia pressure. The third type (van der Waals adsorption) depends only on ammonia pressure. Therefore, the ammonia adsorption amount, V ($\mu mol\,m^{-2}$), can be described as a function of surface organic oxygen content, O_{surf} ($\mu mol\,m^{-2}$), and ammonia pressure, P (kPa), at given temperature:

$$V = s \cdot O_{surf} + w \cdot O_{surf} \cdot P + v \cdot P \quad (1)$$

Where s, w, and v are coefficients indicating strong, weak, and van der Waals interaction.

For all samples, the isotherm was analyzed for the region of ammonia pressure above 30 kPa, where the straight line was observed. The term $s \cdot O_{surf}$ was obtained by extrapolating the isotherm above 30 kPa to the zero pressure.

The relation between $s \cdot O_{surf}$ and surface organic oxygen content, O_{surf}, is shown in Fig. 5. The results give a straight line starting from zero, as was expected. The proportionality constant, s, means a stoichiometry of strongly adsorbed ammonia against surface organic oxygen. Two values, 0.249 (for 1st measurement) and 0.208 (for 2nd measurement), were obtained. The difference between the two values indicates the stoichiometry of ammonia adsorption with extremely strong interaction; $NH_3(a)/O_{surf} = 0.041$.

The term, $w \cdot O_{surf} \cdot P + v \cdot P$, is shown in Fig. 6. The expected relation is well observed with an exceptional case of HNO_3-AC (7.35 $\mu mol\,m^{-2}$ of surface organic oxygen content); the reason is not clear at present. In the case of paired oxygen such as $-NO_2$, only one atom might be effective for this interaction. The intercept of this relation, v, indicates the contribution of van der Waals adsorption which does not depend on the organic oxygen content. As was expected, the

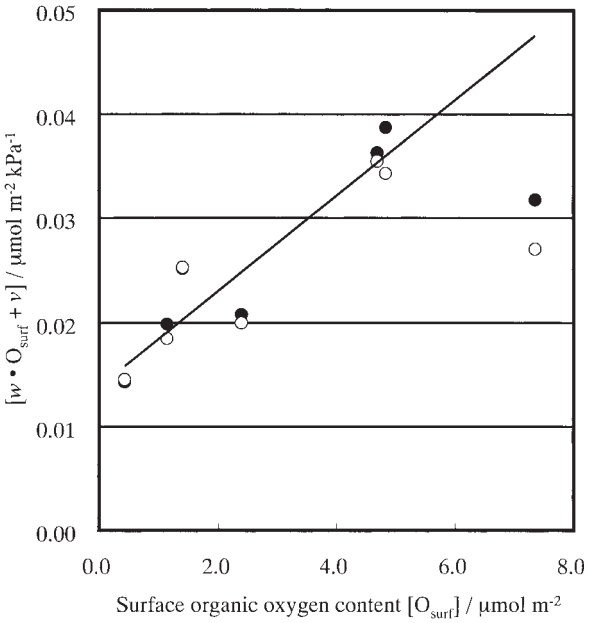

Fig. 6. Surface organic oxygen content dependence on the second and third term (slope of ammonia adsorption isotherm at above 30 kPa) of various surface treated active carbon; (●) 1st measurement, (○) 2nd measurement.

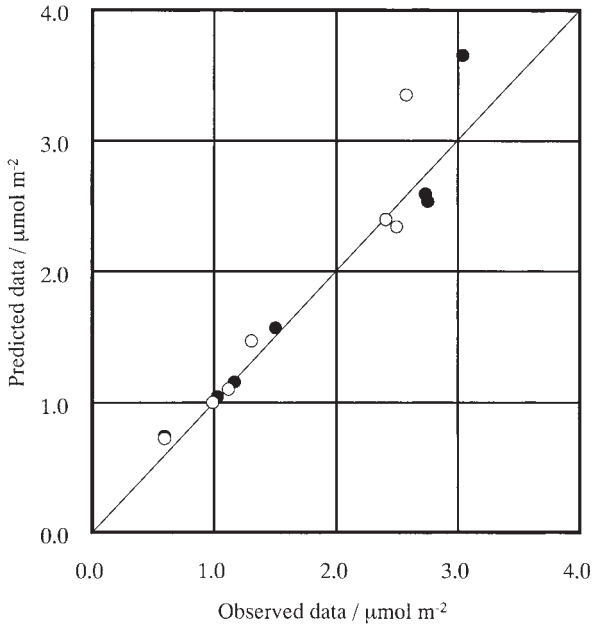

Fig. 7. Comparison between observed data and predicted data of ammonia adsorption amount at 40 kPa and 323 K for surface treated active carbon; (●) 1st measurement, (○) 2nd measurement.

same factor, v, (0.0140 μmol m^{-2} kPa^{-1}) was obtained for 1st and 2nd measurements. The slope of this relation, w, indicates the contribution of weak interaction (probably electrostatic attraction). As was also expected, the same factor, w, (0.00429 kPa^{-1}) was obtained for 1st and 2nd measurements.

Now, the ammonia adsorption amount at 323 K is expressed as follows:

1st isotherm

$$V = 0.249 \cdot O_{surf} + (0.00429 \cdot O_{surf} + 0.0140) \cdot P \quad (2)$$

2nd isotherm

$$V = 0.208 \cdot O_{surf} + (0.00429 \cdot O_{surf} + 0.0140) \cdot P \quad (3)$$

The ammonia adsorption V can be calculated from Eqs. 2 and 3, and compared with the observed data. Figure 7 shows the comparison between observed and predicted (from Eqs. 2 and 3) at ammonia pressure of 40 kPa. Both observed and calculated data correspond well, except for the case of HNO_3-AC. The average relative error was 10%.

Importance of Surface Organic Oxygen for Controlling of Ammonia Adsorption on Active Carbon. In this work, ammonia adsorption on active carbon was adequately explained by the interaction with surface organic oxygen. Generally, active carbon has several kinds of chemical species (oxygen, nitrogen, sulfur, and halogen). Through the hydrogen treatment O, S, and Cl were mostly eliminated; however, N was left as it was. Probably N is located as a part of a graphitic frame. N is not necessary to be exposed on the surface, so ammonia has no chance to interact. Only nitric acid treatment leaves some N atoms; however, this does not seem to relate with ammonia adsorption. Cl was increased with HCl treatment; however, S was not increased with H_2SO_4 treatment. Increased Cl did not increase ammonia adsorption; probably Cl is making the stable lamellar structure.

Surface treatment with HNO_3 or H_2SO_4 must yield surface functional groups such as $\rangle$C=O, –CHO, –COOH, –NO_2, and –SO_3H. However, the concentrations of last two are not much, judging from the elemental analysis (Table 1). In the case of metal nitrate decomposition, the surface is oxidized by nitrate ion in the precursor, and oxygen-containing functional groups must be formed. It is suggested that the contribution of NaOH or CuO to ammonia adsorption is smaller than that of surface functional groups.

Probably there are several kinds of chemical interactions such as ammonium ion formation, electrostatic attraction, or hydrogen bond formation. In this work, we can link the type of chemical adsorption to two kinds of interaction with surface organic oxygen: strong one (independent from ammonia pressure) and weak one (helped by ammonia pressure). It is not the purpose of present study what kind of interaction is the cause. These are the future problems to be studied.

There is another weak (physical) interaction caused with van der Waals force, which is not related with surface organic oxygen, but with the inert surface. This term is also important for active carbon, which can adsorb much ammonia under the high pressure because of the high surface area.

Application of Surface Treated Active Carbon for TSA and PSA in Ammonia Separation. Ammonia separation capacities with TSA method between 323 K (adsorption) and 473 K (desorption) under 40 kPa, are summarized in Fig. 8.[1] Those with PSA method between 40 kPa (adsorption) and 10 kPa (desorption) at 323 K are also shown in Fig. 8. The ammonia separation capacity with TSA was defined as the difference of total adsorption amount between 323 and 473 K.[21] Ammonia desorption temperature of 473 K was selected from

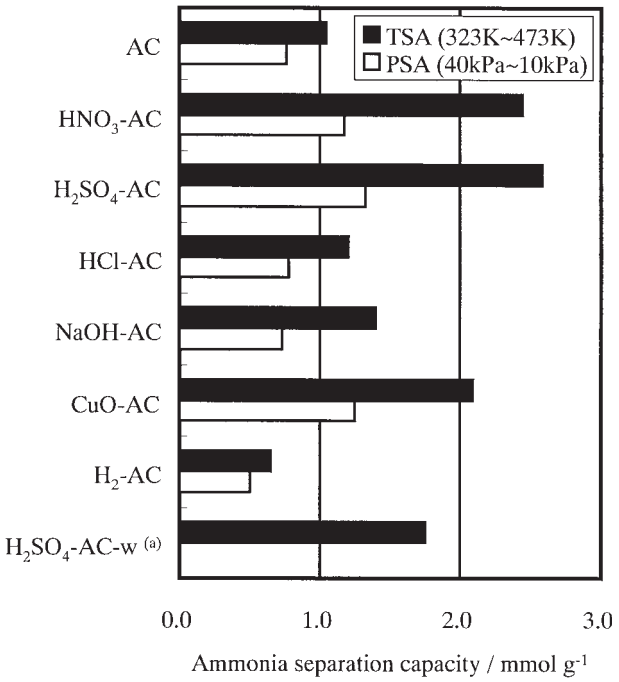

Fig. 8. Ammonia separation capacity of surface treated active carbon for temperature swing adsorption (■) and pressure swing adsorption (□). (a) Previously reported data as reference.[1]

the viewpoint of waste heat utilization of ammonia synthesis (at 623 K). The ammonia separation capacity with PSA was defined as the difference of reversible adsorption amount between 40 kPa and 10 kPa.[21] Here, the difference (separation capacity) comes mostly from weak adsorption and van der Waals adsorption because these are influenced by the pressure.

In the case of TSA method, surface treatment affects ammonia separation capacity much more than in the case of PSA. Because strongly adsorbed ammonia can be separated when the temperature is increased. Oxidized AC (HNO_3-AC and H_2SO_4-AC) has higher ammonia separation capacity among the samples used in this study. Especially the separation capacity of H_2SO_4-AC is 2.58 mmol g^{-1}, and this value is 1.5 times as high as that previously reported (H_2SO_4-AC-w; 1.75 mmol g^{-1}).[1] Though the sample details (sample composition) of H_2SO_4-AC-w are not clear, it is thought that the difference of ammonia separation capacity is derived from the difference of organic oxygen content and the surface area.

In the case of PSA method, oxidized AC (HNO_3-AC and H_2SO_4-AC) and CuO-AC have higher ammonia separation capacity among the samples used in this study. However, the ammonia separation capacities of all such samples were lower than those with TSA method.

Conclusion

In this paper, the behaviors of ammonia adsorption on different types of surface-treated active carbon (HNO_3-AC, H_2SO_4-AC, HCl-AC, H_2-AC, NaOH-AC, and CuO-AC) were studied.

The ammonia adsorption amount of oxidized active carbon (HNO_3-AC, H_2SO_4-AC) and metal nitrate decomposed AC (NaOH-AC, CuO-AC) were higher than that of non-treated AC. It was caused by increasing of surface organic oxygen species as ammonia adsorption site due to these treatments. The adsorption amount on hydrogen-treated active carbon (H_2-AC) was low due to the loss of surface functional groups.

Ammonia adsorption on surface-treated active carbon was distinguished to three types: (1) strong adsorption relating to surface organic oxygen independent from pressure; (2) weak adsorption relating to surface organic oxygen depending upon the pressure; (3) van der Waals adsorption. The former two were further divided to two types: irreversible adsorption and reversible adsorption at 323 K. Ammonia adsorption amount based on this model well represented the data; the average of relative error by the model was 10%. This model can be used for the design of active carbon adsorbents for ammonia.

For the ammonia separation with TSA method between 323 K (adsorption) and 473 K (desorption) at 40 kPa, H_2SO_4-AC had the highest ammonia separation capacity (2.58 mmol g^{-1}) among the samples used in this study.

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