

AMMONIA ADSORPTION ON POROUS CARBONS WITH ULTRAMICROPORE AND ACIDIC FUNCTIONAL GROUPS

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Introduction

A large amount of studies has been reported about the ammonia adsorption on porous carbons [1-7]. The most popular application is deodorant. Recently, ammonia adsorption on charcoals is actively studied especially in Japan [8-10]. Ammonia adsorption is also used for the determination of acidic sites on solid surface by means of temperature programmed desorption (TPD). The surface chemical structure is usually focused on when the adsorption behavior of polar molecules is studied. Tammon et al. [1] have reported the increase of ammonia uptake by addition of acidic functional groups. On the other hand, Domingo-Garcia et al. suggested the importance of micropore on ammonia adsorption; the ammonia strongly physisorbed in micropores caused an error in TPD measurements, when determining surface functional groups on carbon [5]. In the present study, the surface of activated carbon and bamboo charcoal was modified by the liquid phase oxidation using $(\text{NH}_4)_2\text{S}_2\text{O}_8$ and the ammonia adsorption properties were investigated with attention to both pore structure and surface chemical structure.

Experimental

Commercially available activated carbon (AC; Shirasagi, Takeda) and bamboo charcoal (BC) were used. Addition of the acidic functional groups were achieved by oxidation using $(\text{NH}_4)_2\text{S}_2\text{O}_8$ [11]; a 2g sample dried at 383K for 2 h was soaked into a 0.1L aqueous solution of 1 mol/L $(\text{NH}_4)_2\text{S}_2\text{O}_8$ and stirred for a prescribed time at room temperature. The oxidized samples, washed thoroughly and evacuated at 383K over night, were represented by "ox-" and the oxidation treatment time, e.g. ox-AC-48.

Nitrogen adsorption isotherms at 77K were measured by BELSORP28SA (Bel Japan Inc.). The total amount of acidic functional groups (AFG) was determined by Boehm's method [12]. Ammonia adsorption isotherms were measured by BELSORP18 (Bel Japan Inc.) using pure ammonia (99.999%) as follows. After evacuation at 383K below 10^{-1} Pa, the 1st run isotherm was measured at 298K. The sample used for the 1st run was evacuated at 298K under 10^{-1} Pa for an hour and then the 2nd run was performed. The 1st isotherm shows the adsorption on all active sites, while the 2nd isotherm is of physisorbed ammonia which is removable by evacuation at 298K. The difference between 1st run and 2nd run gives an isotherm on chemisorbed sites which have strong potentials preventing desorption by evacuation at 298K.

Results and Discussion

As shown in Figure 1, the amount of AFG on AC increased with oxidation treatment time in $(\text{NH}_4)_2\text{S}_2\text{O}_8$ solution. The amount were increased steeply within 24h and gradually up to 6 days. Porosity parameters determined from the nitrogen adsorption isotherms using α_S -plot [13-15] were listed in Table1. The BET surface area and micropore volumes of AC decreased with time of oxidation treatment, that is, by the increase of AFG, suggesting the blocking of pores by the groups introduced. On the other hand, the introduction of AFG was hardly occurred on BC. It was difficult to measure the nitrogen adsorption isotherms of BC because of a very slow rate of adsorption, indicating the small size of micropores in BC. Therefore, the change of pore structure was estimated by CO_2 adsorption at 298K using Dubinin-Radushkevich plots [16] and the limiting micropore volume is listed in parenthesis in Table 1. The results show no change of micropore volume by oxidation treatment. The hard introduction of functional groups is considered to be due to the narrow micropore and the low external surface area of BC.

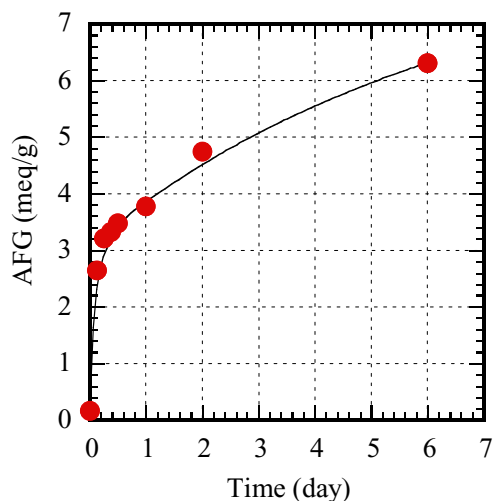


Figure 1. Change in the total amount of acidic functional groups on AC with treatment time in aqueous $(\text{NH}_4)_2\text{S}_2\text{O}_8$ solution.

Table 1 Porosity parameters determined from nitrogen adsorption isotherms (77 K) and the total amount of acidic functional groups (AFG).

Sample	A_{BET} m^2g^{-1}	V_{micro}^* cm^3g^{-1}	A_{ext} m^2g^{-1}	w_{ave} nm	AFG meq g^{-1}
AC	1484	0.564	70	0.75	0.2
ox-AC-3	1292	0.483	82	0.75	2.7
ox-AC-48	1187	0.441	87	0.75	4.8
ox-AC-144	748	0.290	67	0.76	6.3
BC	227	0.089 (0.239)	13	0.78	0
ox-BC-48	-	- (0.239)	-	-	0.3
ox-BC-168	-	- (0.262)	-	-	0.4

A_{BET} : BET surface area, V_{micro} : micropore volume (*micropore volume determined from CO_2 adsorption isotherms at 298 K using DR equation in parenthesis), A_{ext} : external surface area, w_{ave} : average micropore width.

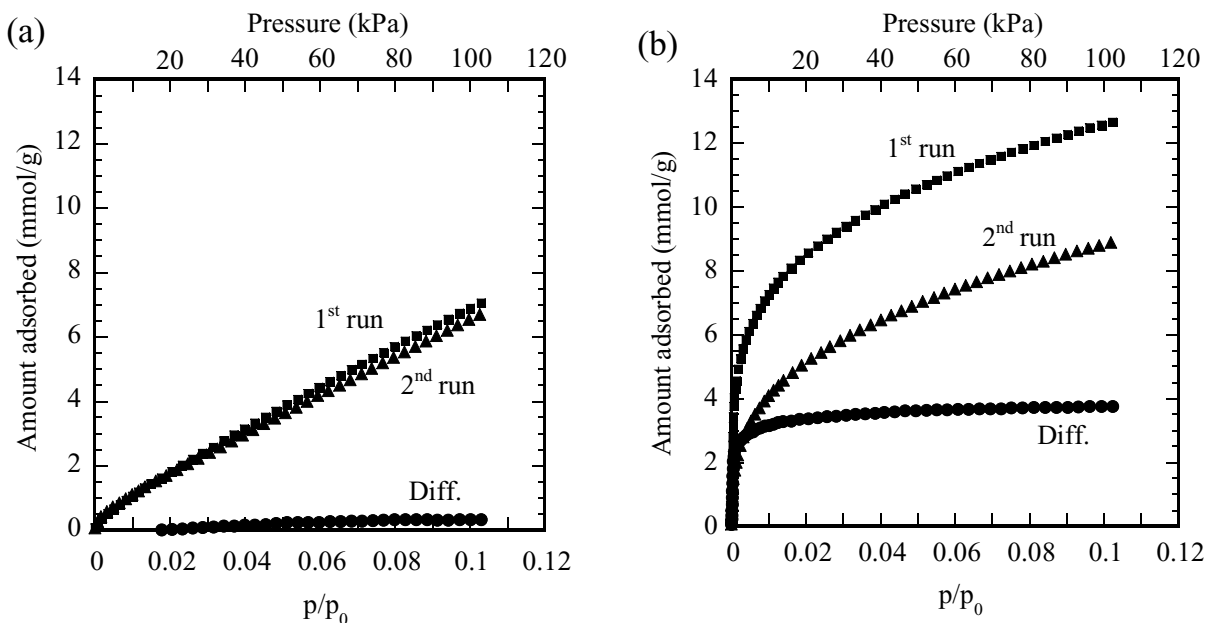


Figure 2. Adsorption isotherm (298 K) of ammonia on (a) AC and (b) ox-AC-48; ■ 1st run after vacuum at 383 K, ▲ 2nd run after vacuum at 298 K, ● difference between 1st run and 2nd run.

Adsorption isotherms of ammonia on AC before and after oxidation treatment are shown in Figure 2. The total ammonia uptake in the 1st run isotherm was drastically increased by oxidation treatment at the relative pressure range less than 0.1. One of the reasons is the increase of chemisorbed ammonia, as shown by the difference between the 1st and 2nd run isotherms. The chemisorbed ammonia formed the salt with acidic functional groups by molar ratio of 1:1; the amount of chemisorbed ammonia ($V_{0.1\text{-Chem}}$) in Table 2 had a good correlation with the amount of acidic functional groups measured by Boehm's method. It is thought that the lower amount of $V_{0.1\text{-Chem}}$ than AFG is due to the existence of lactone-type functional groups which are counted by hydrolysis in aqueous alkaline in the procedure of Boehm's method but not in gas phase chemisorption.

Additionally, the potential of ammonia physisorption also increased by oxidation as seen in the change of 2nd run isotherms before and after oxidation. The 2nd run isotherms were analyzed based on the BET equation;

$$v = \frac{v_m C p}{(p_0 - p)[1 + (C - 1)(p/p_0)]} \quad (1)$$

where v is the amount adsorbed at pressure p and v_m represents the amount of monolayer adsorption. The constant C reflects the strength of physisorption potential. The BET plots on AC before and after oxidation are shown in Figure 3 and the parameters are listed in Table 2. The parameter C indicates the increase of physisorption potential with increasing functional groups. The higher potential of physisorbed ammonia is thought to be due to the addition of acidic functional groups, the polar sites which act as primary adsorption center of ammonia physisorption. The results mean that the introduction of acidic functional groups caused not only an

Table 2. The ammonia adsorption parameters at 298 K.

sample	$V_{0.1\text{-Chem}}$ mmol g^{-1}	$A_{\text{BET-Phys}}$ $\text{m}^2 \text{g}^{-1}$	v_m $\text{cm}^3 \text{g}^{-1}$	C
AC	0.3	1877	499	4
ox-AC-3	2.1	884	235	29
ox-AC-48	3.8	841	224	39
ox-AC-144	5.3	722	192	50
BT	0.3	396	105	53
ox-BT-48	0.5	397	105	76
ox-BT-168	0.5	410	109	67

$V_{0.1\text{-Chem}}$: amount chemisorbed at $P/P_0=0.1$ calculated from the difference between 1st run and 2nd run isotherms, $A_{\text{BET-Phys}}$: BET surface area determined from 2nd run isotherm, v_m , C : parameters from BET plot of 2nd run isotherm.

increase of chemisorbed ammonia but also the improvement of physisorption properties at the low relative pressures.

The bamboo charcoal showed higher potential of ammonia physisorption than the activated carbon without oxidation, though the ammonia adsorption ability was unchanged by liquid phase oxidation because acidic functional groups were hardly introduced on the BC surface. The higher physisorption ability is considered to be attributable to the ultramicropores which originally exist in BC because the isotherm is similar to that of molecular sieving carbons which have ultramicropores with the diameter of 0.4-0.5nm [17, 18].

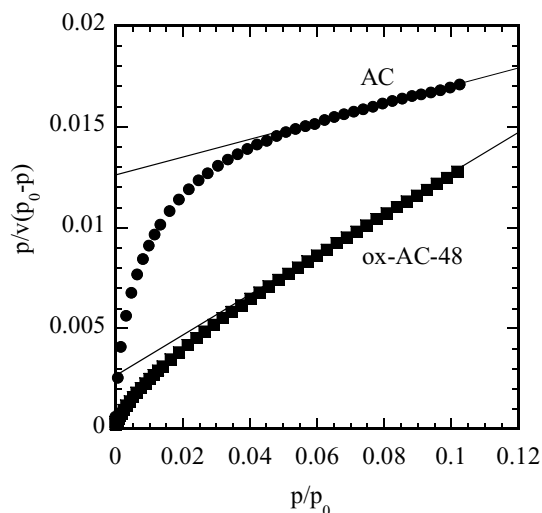


Figure 3. BET plots of ammonia physisorption (2nd run) on AC and ox-AC-48.

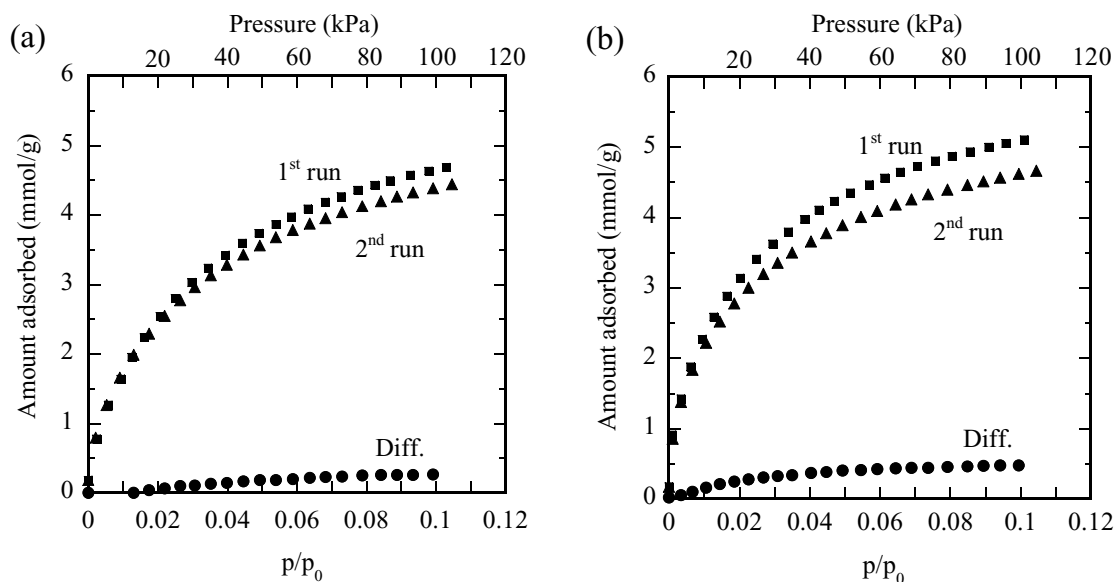


Figure 4. Adsorption isotherm (298 K) of ammonia on (a) BC and (b) ox-BC-48; ■ 1st run after vacuum at 383 K, ▲ 2nd run after vacuum at 298 K, ● difference between 1st run and 2nd run.

Conclusions

The amount of acidic functional groups on activated carbon increased with treatment time in $(\text{NH}_4)_2\text{S}_2\text{O}_8$ solution. The introduction of acidic functional groups caused an increase of chemisorbed ammonia as well as the improvement of physisorption properties at low relative pressures. The chemisorbed ammonia formed the salt with acidic functional groups by molar ratio of 1:1; the amount of chemisorbed ammonia had a good correlation with the amount of acidic functional groups measured by Boehm's method. The higher potential of physisorbed ammonia is due to the addition of acidic functional groups which act as polar sites for ammonia adsorption. On the other hand, the bamboo charcoal showed higher potential of ammonia physisorption than the activated carbon without oxidation, though the ammonia adsorption ability was unchanged by liquid phase oxidation because acidic functional groups were hardly introduced on the surface. The higher adsorption ability of the bamboo charcoal is considered to be attributable to the ultramicropores because the physisorption potential was similar to that of molecular sieving carbons.

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