[Chem. Pharm. Bull. 36(5)1919—1921(1988)]

Preparation of Plasma-Treated Activated Carbon Suitable for Ammonia Adsorption

SEIKI TANADA,* SHOZO TSUTSUI, KEITO BOKI, and TAKEO NAKAMURA

Faculty of Pharmaceutical Sciences, Kinki University, Kowakae 3-4-1, Higashi Osaka, Osaka 577, Japan

(Received September 18, 1987)

The adsorption characteristics of ammonia on several kinds of plasma-treated activated carbon (PT-AC) prepared under different treatment conditions were investigated from the adsorption isotherms, characteristic energy, and isosteric differential heats of adsorption. The amount of acid functional groups of the PT-ACs was increased by 8—70% compared to that of raw activated carbon (R-AC) by plasma treatment. The amount of acid functional groups on the PT-ACs increased with increase in oxygen pressure, reached a maximum at a pressure of 1.0 Torr and then decreased. The adsorption capacity, the characteristic energy, and the isosteric differential heats of adsorption for ammonia of No. 4 (treated at 1.5 Torr) were the greatest among the PT-ACs and R-AC. From the characteristic energy and heat of adsorption, it appeared that the acid functional groups were formed by the oxygen plasma treatment into micropores and super-micropores of activated carbon. It is concluded that the treatment conditions of No. 4 produced a characteristic adsorbent material having the greatest adsorption capacity for ammonia among the PT-ACs.

Keywords——ammonia; oxygen plasma; acid functional group; plasma treated activated carbon; plasma treatment condition; characteristic energy; adsorption isosteric differential heat

Ammonia, which is often discharged into the atmosphere from carcass processing plants, sewage treatment plants, *etc.*, is both malodorous and toxic.[1] Ammonia can barely be removed by the gas wash method[2] and the contact oxidation method.[3] It is necessary therefore to establish an adsorption method for the removal of ammonia. In adsorption methods, the adsorption capacity of the adsorbent is one of the vital factors. We clearly need to develop a form of activated carbon which has an excellent adsorption capacity for ammonia.

In a previous paper, we reported that ammonia could be effectively removed by plasma-treated activated carbon (PT-AC).[4] However, the characteristics of substances modified by plasma are markedly altered by the treatment pressure.[5] In this study, several PT-ACs having different physicochemical properties were prepared and the adsorption characteristics of ammonia were investigated on the basis of the amount adsorbed, the application of the two-term adsorption equation to the adsorption to the adsorption isotherms, and the isosteric differential heats of adsorption.

Experimental

Materials——The ammonia gas used was of certified grade from Seitetsu Kagaku Co. Raw activated carbon (R-AC) was obtained commercially from Bamberg Co., Technicol, and its characteristics included a wide micropore volume distribution. Details of the plasma apparatus of inductive coupling type have been described previously.[4] The specific surface area of the activated carbon was measured by the nitrogen BET method.[6] The concentration of surface functional groups on the activated carbon was measured by Boehm's method.[7]

Procedure for Adsorption——Adsorption isotherms of ammonia on the activated carbon were determined in an

all-glass vacuum system of the type described previously.[8] The equilibrium amounts adsorbed at pressures up to 600 Torr were measured using a BET apparatus with a spring balance.

Results and Discussion

Table I shows the treatment conditions with plasma, as well as the specific surface area, pore volume, and amount of acid functional groups. The micropore volumes of the PT-ACs were about the same or smaller than that of R-AC. The amounts of acid functional groups on the PT-ACs increased with treatment time. Moreover, the amounts of acid functional groups on the PT-ACs increased with increase in oxygen pressure, reached a maximum at a pressure of 1.0 Torr and then decreased. These results indicated that the ashing amounts of acid functional groups on PT-ACs are larger than the amounts of acid functional groups produced on PT-ACs at treatment pressures above 1.0 Torr. Clearly, the chemical properties of the PT-ACs were markedly altered by the treatment time and pressure. Figure 1 shows adsorption isotherms of ammonia on R-AC and PT-ACs. The adsorption capacity of ammonia on each of the PT-ACs was greater than that on R-AC in the range of less than 600 Torr. In particular, the adsorption capacity of ammonia on No. 4 was greatest among all the PT-ACs. Moreover, to clarify the adsorption characteristics of ammonia on the PT-ACs, the two-term adsorption equation[9] was applied to the adsorption isotherms of ammonia on R-AC and the PT-ACs.

TABLE I. Physicochemical Properties of R-AC and PT-ACs

Adsorbent No.	Plasma treatment conditions: Oxygen pressure (Torr)	Plasma treatment conditions: Time (h)	Surface area (m^2/g)	Pore volume (100 Å < r) (ml/g)	Micropore volume (15 Å < r) (ml/g)	Amount of acid functional groups (meq/g)
1 R-AC	0.0	0.0	1368.5	0.7293	0.4699	0.741
2 PT-AC	0.5	3.0	1315.0	0.7550	0.3970	0.897
3 PT-AC	1.0	3.0	1365.9	0.7503	0.4711	1.244
4 PT-AC	1.5	3.0	1309.2	0.7209	0.4651	1.221
5 PT-AC	3.0	3.0	1221.3	0.7091	0.3494	1.097
6 PT-AC	4.5	3.0	1164.5	0.6484	0.4205	0.890
7 PT-AC	1.5	1.0	1422.5	0.7365	0.4620	0.885
8 PT-AC	1.5	2.0	1100.5	0.6454	0.4305	1.009
9 PT-AC	3.0	0.5	1258.2	0.6826	0.4452	0.938
10 PT-AC	3.0	2.0	1232.8	0.6749	0.4300	1.007

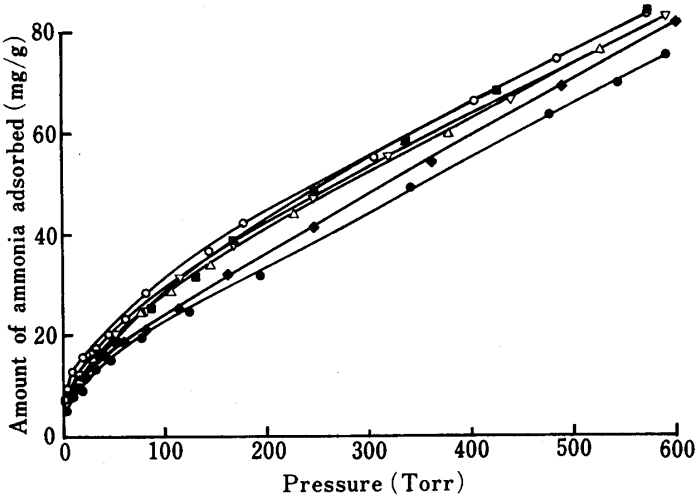

Fig. 1. Adsorption Isotherms of Ammonia on Raw Activated Carbon and Plasma-Treated Activated Carbon at 20 °C

●, No. 1; ■, No. 2; △, No. 3; ○, No. 4; ◆, No. 5; ▽, No. 6.

The results indicated that the adsorption sites of ammonia on R-AC and the PT-ACs consisted of micropores and supermicropores. The characteristic energy was calculated from the slopes of the straight lines of the plots of the two-term equation. The value of the characteristic energy of No. 4 (16800 cal/mol) was 1.15 times larger than that of R-AC and was the greatest among all the PT-ACs. Moreover, in the initial stage of adsorption, the isosteric differential heat of adsorption of ammonia on No. 4 was approximately 1.5 times larger than that on R-AC. The adsorption behavior of ammonia on No. 4 and R-AC differed markedly in the initial stage of adsorption; that is, the adsorption behavior of ammonia in the micropores of No. 4 was different from that of R-AC. It is concluded that the treatment conditions of No. 4 formed abundant acid functional groups in micropores and so produced a characteristic adsorbent material having the greatest adsorption capacity for ammonia among the PT-ACs.

References

1) A. Sakamoto, Y. Ikawa, and M. Inoue, *Wakayamaken Eisei Kenkyusyo Nempo*, **18**, 113 (1970).
2) J. Kutsuma, K. Sakurai, I. Koyama, T. Ishiguro, and T. Ohira, *Tokyoto Kogai Kenkyusyo Nempo*, **1**, 140 (1970).
3) K. Araki and S. Honda, *Hokkaidoritsu Kogyo Sikenzyo Hokoku*, **230**, 9 (1974).
4) S. Tanada, S. Tsutsui, K. Boki, and T. Nakamura, *Chem. Pharm. Bull.*, **35**, 3433 (1987).
5) Y. Nagata, "Purazuma Zyugo," Tokyo Kagaku Doujin Co., Ltd., Tokyo, 1986, pp. 247—248.
6) K. Boki, *Jpn. J. Hyg.*, **32**, 482 (1972).
7) H. P. Boehm, *Angew. Chem., Int. Ed. Engl.*, **5**, 533 (1966).
8) S. Tanada and K. Boki, *Chem. Pharm. Bull.*, **22**, 2703 (1974).
9) M. M. Dubinin, *J. Colloid Interface Sci.*, **46**, 351 (1974).