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Evaluation of n-butane Gas Adsorption Performance of Composite Adsorbents Used for Carbon Canister

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Abstract

A novel adsorbent design technique was proposed to composite adsorbent used for carbon canister for improving the adsorption performance of n-butane gas. Two kinds of activated carbons were tested to produce composite adsorbents and evaluate the performance by measuring the adsorption isotherms of butane and pore structure characteristics. The volume-based amount of adsorption for the adsorbents prepared at sodium silicate solution concentration of 0.1wt% is 1.04 and 1.53 times that of the raw activated carbons (AC1 and AC2). The packing density of the composite adsorbent increased with the increase of sodium silicate solution concentration.

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1. Introduction

Road transport is a major source of hydrocarbon emissions. Volatile organic compounds (VOC) from gasoline evaporative emissions are ozone precursors and contribute thus to ground-level ozone. The major volatile components of gasoline are hydrocarbons, such as n-butane, pentane, and propane. These hydrocarbons are evaporated by the heat from the outside air when a vehicle is parked for a long period of time and are also emitted from the fuel tank during refueling. These volatile fuel gases are known to have

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toxic effects on the human body. For this reason, fuel emissions regulations have been introduced to control and regulate the emissions of such components. Carbon canister is an evaporative emission control device to prevent the release of evaporative fuel gas from gasoline tank by the gas adsorption with activated carbon [1-4].

With the tighter control on exhaust emissions from gasoline-fuelled vehicles, the improvement of carbon canister performance is urgent and crucial concern. Especially, the adsorption capacity improvement of activated carbon used in canister is one of the key issues.

To improve the performance of carbon canister, Sato et al. [5, 6] conducted basic experiments and calculations to reveal the behavior of gas diffusion caused by the concentration difference of adsorbed gas in carbon packed bed for estimating the gas diffusion by numerical calculation. Seto et al. [7] confirmed the pore blockage of the deteriorated activated carbon, developed a new activated carbon that is difficult to blockage and the 2.5~4nm pores that can effectively adsorb the gasoline vapour increase.

But the above studies are about the improvement of the durability, the study of the adsorption capacity improvement is little. In this study, we focused on the research of adsorption capacity of the adsorbent, and proposed a novel adsorbent design technique to composite adsorbent used for improving the evaporative vapour adsorption performance of carbon canister. To have a reasonable design and manufacturing method is the purpose of starting this thesis. In the process, the composite adsorbent was prepared after silica gel was synthesized in the pores of activated carbons by impregnating activated carbons in sodium silicate solution. And the performance was evaluated by measuring the adsorption isotherms of n-butane gas which is the major component of evaporative fuel gas and pore structure characteristics.

2. Experimental

2.1. Materials

Two kinds of activated carbons (AC1: specific surface area $1950\text{m}^2/\text{g}$ and AC2: the specific surface area: $1190\text{m}^2/\text{g}$, and each particle diameter adjusted at about $100\mu\text{m}$) with different pore distribution were used. As shown in Figure 1, the pores of AC1 widely develop from mesopore to macropore. The pores of AC2 mainly develop in micropore. The properties and pore structure characteristics of two adsorbents were shown in Table 1. As shown in Table 1, two type activated carbons with high specific surface area were used.

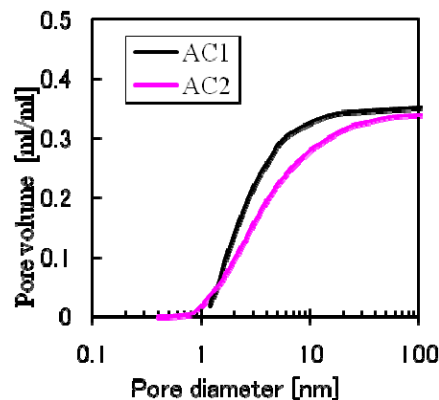


Fig. 1. Pore distribution of raw samples

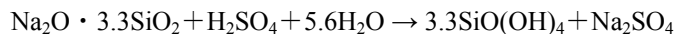
Table 1. Properties of raw samples

	AC1	AC2
Specific Surface Area [m ² /g]	1950	1190
Meso, Macro Pore Specific Surface Area [m ² /g]	1590	1023
Micro Pore Volume [ml/g]	0.22	0.11
Micro Pore Specific Surface Area [m ² /g]	360	167
Packing Density [g/ml]	0.260	0.247

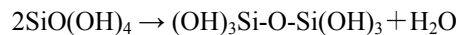
2.2. Procedure and evaluation methods

The scheme for impregnating the hydrophilic silica is shown in Fig. 2. The Scheme for impregnating the hydrophilic silica is shown in Figure 2. A similar process [8, 9] was used to impregnate silica into activated carbons. To prevent the dissolution of silicic acid from the activated carbon, the neutralization process of sodium silicate was divided into two stages: 1) Activated carbon was impregnated with a sufficient amount of sodium silicate and dried, then 2) sulphuric acid was added.

A silica monomer was made from sodium silicate and sulphuric acid by the following reaction:



After heating up and aging, the following dehydrate-condensation reaction occurred:



These processes formed an adherent silica layer onto the pore surface of activated carbon.

The impregnating temperature was set at 298K which was the best temperature. Samples were made in various experimental conditions (sodium silicate solution concentration of 0.1~10wt%, impregnating time of 1~48h). The adsorbent properties were evaluated by adsorption isotherms, pore size analysis, surface observation and packing density. The pore structure characteristic and the packing density of samples were evaluated by water vapor adsorption isotherms in 298K (BELSORP18, Bell Japan, Inc., Osaka, Japan) and N₂ gas adsorption method in 77K (AUTOSORB-1, Yuasa Ionics Co., Ltd., Osaka, Japan). Surface area was obtained by the Brunauer-Emmett-Teller (BET) method. Pore volume was calculated from the results of water vapor adsorption isotherms. Adsorbent appearance was observed by a SEM-EDX (scanning electron microscope & Energy Dispersive X-ray Spectrometer (JSM-5600LV by JOEL, Tokyo, Japan).

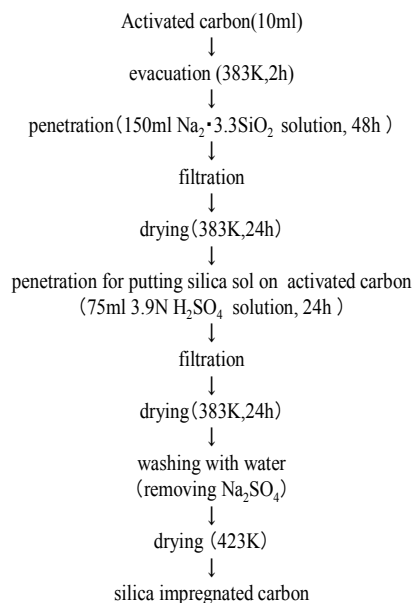


Fig. 2. Scheme of impregnating hydrophilic silica process

3. Results and Discussion

3.1. SEM-EDX images of silica impregnated carbon

SEM-EDX images of AC1 raw samples and AC1's 1wt% silica impregnated carbon were shown in Figure 3. In EDX photo, silica is shown as red part. Just as the picture shown, we can find out the existence of silica within AC1's raw carbon, and can tell the main carbon element. The existence of silica can be observed within AC1's 1wt% silica impregnated activated carbon. Especially when at 10wt% condition, the red part is increasing, and large amount of silica can be observed. According to the results above, it is possible to confirm the adding of silica within activated carbon pore. To sum up, when the sodium silicate solution concentration is high, it is easy for sodium silicate's molecule to infiltrate into activated carbon minute hole.

3.2. *n*-Butane adsorption isotherms of silica impregnated carbon

The *n*-butane adsorption isotherms of the samples obtained from AC1 in the condition of sodium silicate solution of 0.1, 1, 10wt% and impregnating time of 48h were shown in Figure 4, compared with those of raw activated carbons. Even in a lower pressure environment, we can see a large amount of *n*-butane's adsorption. When sodium silicate solution concentration is 1wt%, *n*-butane's adsorbed amount increased by maximum of 1.07 times than the raw carbon in the relative pressure of 0.4. When it is 0.1wt%, *n*-butane's adsorbed amount increased by maximum of 1.04 times than the raw carbon. When it is 10wt%, *n*-butane's adsorbed amount decreased by maximum of 17% than the raw carbon.

A similar tendency was observed for other impregnating conditions and even for AC2 applied shown in Figure 5. When it is 0.1wt%, *n*-butane's adsorbed amount increased by maximum of 1.53 times than the

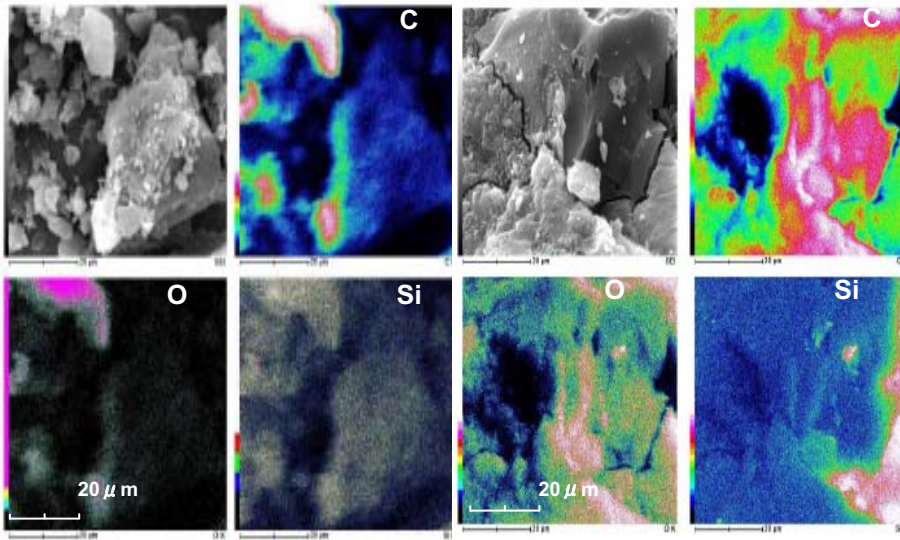


Fig. 3. SEM-EDX images of AC1 (left) and AC1 + 1wt% (right)

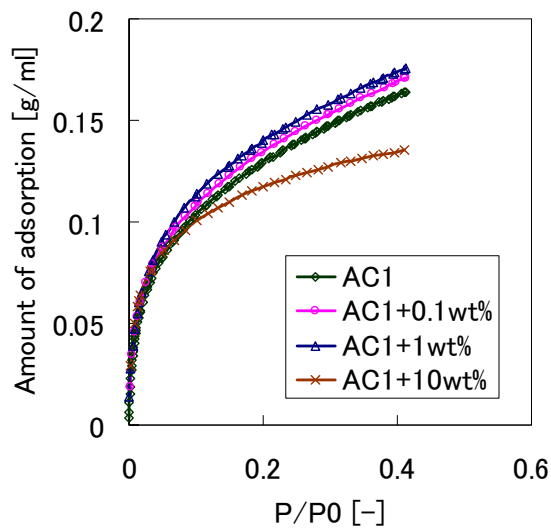


Fig. 4. Adsorption isotherms of n-butane at 298K, AC1

raw carbon in the relative pressure of 0.4. When it is 1wt%, n-butane's adsorbed amount increased by maximum of 1.11 times than the raw carbon. When it is 10wt%, n-butane's adsorbed amount decreased by maximum of 7% than the raw carbon.

According the results above, when the condition of sodium silicate solution are 0.1 and 1wt% respectively, we can say that n-butane's adsorption performance of silica impregnated carbon is larger than raw carbon.

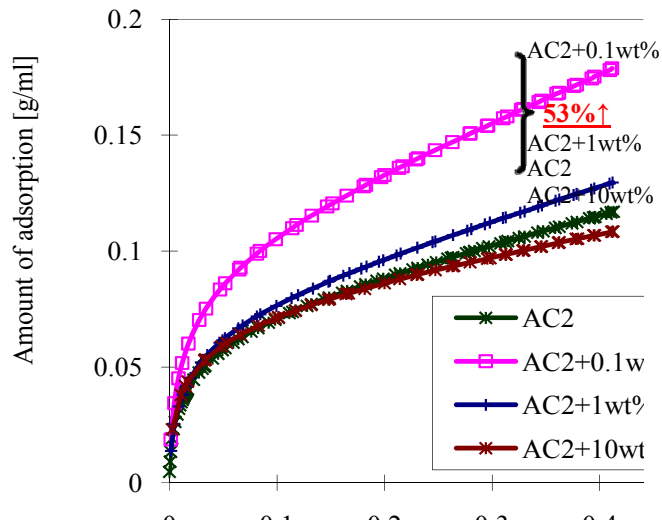


Fig. 5. Adsorption isotherms of n-butane at 298K, AC2

3.3. Pore structure

The pore distribution of AC1-derived sample was shown in Figure 6. From figure, it is observed that the pore distribution is different depending on sodium silicate solution concentration. That is to say, the increase and decrease of the pore volume can be confirmed. Under the condition sodium silicate solution is 0.1, 1wt%, the pore volume of impregnated sample increased overall compared with the raw sample. On the other hand, under the condition of 10wt%, the pore volume of the impregnated sample decreased overall compared with the raw sample. This is thought to be one of the factors that n-butane adsorption capacity of 0.1, 1 wt%-impregnated sample improved and that of 10wt% dropped down compared with the raw sample.

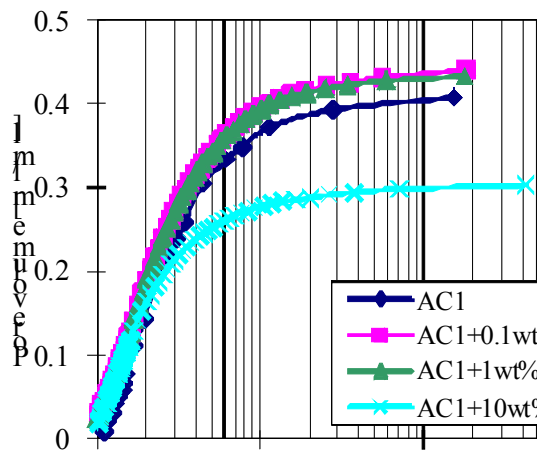


Fig. 6. Pore distribution of AC1

3.4. Packing Density

The packing density and pore structure characteristics of two adsorbents were shown in Table 2. As shown in Table 2, the specific surface area of the impregnated sample decreased, mesoporous and macroporous specific surface area decreased, microporous specific surface increased with the increase of sodium silicate solution concentration. The packing density of impregnated sample increased with the increase of sodium silicate solution concentration. For AC1, the packing density of 10wt% impregnated sample increased by maximum of 1.4 times than the raw sample. For AC2, shown the same tendency as AC1, the packing density of 10wt% impregnated sample increased by maximum of 1.3 times than the raw sample. According the results above, the increase effect of microporous volume and packing density of impregnated sample with the pore size narrowing can be confirmed.

Table 2. Properties of samples prepared by impregnating of silica into activated carbon pores

Sample	Surface area [m ² /g]	Meso, Macro pore surface area [m ² /g]	Micro pore volume [ml/g]	Micro pore surface area [m ² /g]	Packing Density [g/ml]	Amount of adsorption in P/P0=0.4 [g/ml]
AC1	1950	1586	0.22	360	0.260	0.162
AC1+0.1wt%	1700	1347	0.25	364	0.274	0.169
AC1+1wt%	1650	1280	0.25	371	0.281	0.173
AC1+10wt%	1240	595	0.30	646	0.364	0.134
AC2	1190	1023	0.11	167	0.247	0.115
AC2+0.1wt%	1056	957	0.12	99	0.267	0.175
AC2+1wt%	930	825	0.12	105	0.290	0.127
AC2+10wt%	830	534	0.14	296	0.320	0.107

4. Conclusions

To improve n-butane adsorption performance of adsorbent applied in carbon canister, preparation of composite adsorbents was performed by impregnating silica into the pores of activated carbon. The following conclusions were obtained.

- 1) The volume-based amount of adsorption for the adsorbents prepared at sodium silicate solution concentration of 0.1wt% and impregnating time of 48 h are 1.04 and 1.53 times that of the raw activated carbons (AC1 and AC2), respectively.
- 2) The volume-based amount of adsorption for the adsorbents prepared at sodium silicate solution concentration of 0.1wt% and impregnating time of 48 h are 1.04 and 1.53 times that of the raw activated carbons (AC1 and AC2), respectively. The volume-based amount of adsorption decreased under the condition of 10wt% of sodium silicate solution concentration and 48h of impregnating time.
- 3) The packing density of the composite adsorbent increased with the increase of sodium silicate solution concentration.

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