Cold Plasma Treatment of Activated Carbon and its Surface Properties

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We have developed a cold plasma heat - treatment technique through which activated carbon powders having a large specific surface area can be prepared in a short period of time.   In this method powders were heated by cold plasma induced by microwave of 2.45GHz under vacuum.   Four kinds of coconut shell based activated carbon powders were used as samples.   The specific surface area of the samples were increased by plasma heat - treatment to a value of over $2000m^2/g$.   It became apparent by observing SEM photographs that dust and particles in the macropores of samples prepared by plasma heat - treatment were reduced more than those prepared by conventional heating in an electric furnace under vacuum.   In addition, as observed by AFM as a result of the surface morphology of samples prepared by plasma heat - treatment many fine bubble - like formations were formed on the surface of the sample.   When we measured the amount of several organic compounds adsorbed on the surface of the sample, there appear an improvement in the adsorption properties of the samples that had been prepared by plasma heat - treatment.   In particular, the amount of carbon disulfide adsorbed on the surface of the sample was increased remarkably by plasma heat - treatment.   This result suggests that the surface properties of the sample were improved by plasma heat - treatment.

1. Introduction

Activated carbon has been used as an adsorbent in the gas - phase or the liquid - phase since ancient times and it is one of the adsorbents used in the widest range. Activated carbon has been widely used in every industry such as for the removal of environmental pollutants.   Activated carbon has many pores and these pores contribute to the extension of its specific surface area.   In order to the increase the number of pores in organic raw materials, heat - treatment methods using H_2O vapor or CO_2 or chemical treatment methods using zinc chloride and phosphoric acid of have been used since ancient times [1] .

Recently a new treatment technique which can add new functional properties to activated carbon have been developed.   For example, there is a method for the preparation of activated carbon with a specific surface area of $3000m^2/g$.   In this method which was developed by Yamaguchi et al. [2] a sample is heated in a large excess of alkali solution.   Studies to improve the adsorption selectivity as has been progressed.   V.R.Deitz et al. [3] found an improvement in the adsorption selectivity against CH_3I of activated carbon when it was treated by triethylenediamine.   Ikeda et al. [4] reported that when activated carbon was treated by I_2- KI, the amount of Hg vapor adsorbed on the surface was increased.

Continuing this line of research, we have developed a process that can prepare and surface treat many fine powders in a short period of time using a cold plasma induced by microwave[5-9]. For example it is a characteristic of magnesia, silica, etc. metal oxide fine powders prepared by this method to have a large specific surface area.

Plasma is a gas of the electrolytic dissociation state and it has a high reactively. Plasmas are classified by temperature into thermal plasma and cold plasma[10]. Thermal plasma has temperature of over several 1000K and has been used to make fine powders[11]. On the other hand, since the temperature of cold plasma is only about a few 100K[12], it is a necessary reaction source for the manufacturing process of IC chips.

Using cold plasma for treatment of activated carbon is of great interest, because it is expected that activated carbon which has new properties can be prepared. The microwave cold plasma heat technique which has been developed by us consists of two heat principles. One of the principles is heat from inside the sample by dielectric microwave heating. Another principle is heat by plasma of H_2O molecules etc.which is released from the sample. High heating efficiency is characteristic of this method. Therefore, the effects of cold plasma heat - treatment are expected in a short time.

In this report, we investigated the surface properties of activated carbon powder prepared by microwave cold plasma heat - treatment, and revealed the peculiarities of the surface morphology and adsorption properties of the sample.

2. Experimental

2.1 Microwave cold plasma heat - treatment

The microwave cold plasma heat - treatment apparatus is shown in Fig.1. Using this apparatus, all types of metal oxide fine powders can be prepared and their surface properties are improved in a short time. This apparatus consists of a microwave generator (MR - 1991T, Ewig), an isolator, a power monitor, an impedance adjustment unit, an applicator, a depressure vacuum pump and a liquid N_2 trap.

The output frequency of the

Fig.1 Schematic diagram of microwave-induced plasma heating apparatus

microwave was 2.45GHz and the output power could be varied from 0 to 1000W. The power monitor was provided with output meters for both incident and reflected waves, the difference between the reading of these meters was considered the microwave output power at the time of plasma heating.

In the applicator, which is the sample heating unit, a quartz round bottom flask attached to obstructive boards(capacity 200mℓ) was used as the reactor. It was connected to a mechanical stirrer and the reactor was rotated at 60rpm so that the powder samples could be heated uniformly.

The following is the plasma heating method process. (1)The reactor was charged with an activated carbon sample. (2) The internal pressure of the reactor was lowered with the vacuum pump, within the range of 0.01 - 0.1Torr. (3)Microwaves
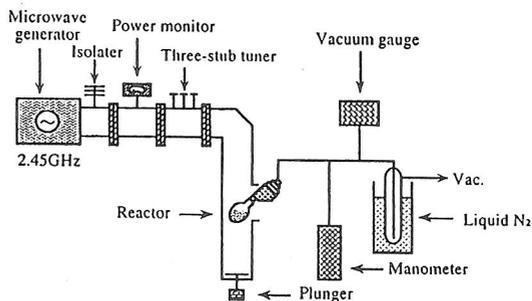
of a predetermined output(200 - 400W) were applied to the reactor, and a plasma was generated. (4)The impedance was adjusted at this time in order to increase the efficiency of sample heating. The three - stub tuner and plunger were adjusted to minimize the power of reflected waves. (5)Cold plasma was generated in the reactor and microwave irradiation was stopped after a predetermined period of time(1 - 5min). (6)The sample was taken out of the reactor.

2.2 Evacuation heat - treatment

The following is the evacuation heat - treatment process. (1)The quartz reactor was charged with the sample. (2)The reactor was heated within the range 120 - 800 ℃ by a electric furnace. At the same time, the internal pressure of the reactor was lowered to about 1×10^{-5} Torr with the vacuum pump. (3)The treatment was stopped after one hour when the reactor was at a predetermined temperature. (4)The sample was taken out of the reactor.

2.3 Samples and physical property measurements

The activated carbon powders used for samples were coconut shell based. These samples were A (Kuraray Coal GG, Kuraray Chemical Co.), B (Yashi coal, Taihei Kagaku Co.), C (Shirasagi G₂ CS, Takeda Chemical Industriers.) and D (Tsurumicoal HC - 16, Tsurumicoal Co.). Sample properties are shown in Table.1. These samples have a specific surface area of 1400 - 1650m^2/g and were used mainly for gas - phase adsorption.

Table. 1 Property of raw materials

Sample	Surface area ($m^2 g^{-1}$)	Weight[a] loss (wt%)
A	1617	3.5
B	1637	1.9
C	1489	1.1
D	1421	3.5

a) It mean water on surface of sample and mesured by Japan industrial standard.

In this experiment, sample A was picked as a representative sample, to investigate the relation between the condition of microwave cold plasma heat - treatment and the surface properties of the sample. Evacuation heat - treatment samples were used as a reference.

The specific surface area of sample prepared by microwave cold plasma heat - treatment, evacuation heat - treatment and of the untreated raw material were determined by the BET method using N₂ gas adsorption. As with previous treatment of the measurement of specific surface area, the sample was heated to 120 ℃ under vacuum for one hour.

The surface form of sample prepared by microwave cold plasma heat - treatment, by evacuation heat - treatment and of the untreated raw material were observed using scanning electron microscope(SEM) and an atomic force microscope(AFM). Usually, when observing powders with AFM, powder is formed into pellets [13,]. In this case, however, this might cause defects on the surface of the powder. Therefore, we devised an observation method in which the powder is fixed on a holder using an adhesive preventing defects on the surface of the powder [14]. In this investigation, the surface morphology of the sample was observed using this technique.

The amount of carbon disulfide, benzene, ethyl acetate and toluene adsorbed on the surface of samples prepared by microwave cold plasma heat - treatment and of the untreated raw material were investigated.

3. Results and Discussion

3.1 Microwave cold plasma heat - treatment and specific surface area

Various activated carbon samples were treated by cold plasma heating and the

specific surface area was measured.   Fig.2
shows the results of the examination relating
to microwave output power and specific
surface area when treatment time was fixed
at 2min.   When the microwave output was
adjusted to 300W, a maximum specific
surface area for each sample was obtained.
The increases were in the range of 20 - 40%.

The effect of cold plasma treatment was
examined in detail using sample A which
could obtain the largest specific surface area
by cold plasma heat - treatment.   Fig.3
shows the results of the examination relating
to treatment time and specific surface area
when microwave output power was fixed
300W.   Specific surface area of the sample
reached a maximum of 2626m^2/g after a
very short treatment time of 1min.
However, excess heat - treatment decreased
the specific surface area of the samples.

As a control experiment, activated carbon
samples were treated by the usual
evacuation heat method.   The reactor was
put into an electric furnace and was heated
at various temperatures under vacuum for
1hr.   The results of specific surface area
measurement of samples prepared by
evacuation heat treatment are shown in
Fig.4.   When samples were treated at 600
°C , a maximum specific surface area of
2091m^2/g was obtained.   According to
data obtained by both heat methods, it was
found that the plasma heat method can heat
a sample with a higher efficiency than can
the electric furnace heat method.

Activated carbon has several types of
surface pores such as micropore, mesopore
and macropore, and these pores can be
formed by heating raw materials to about 800
°C[16] . The temperature of plasma generated
under this plasma heater treatment condition
is about 800°C[16] .   The generated plasma
is at a suitable temperature for formation of
pores.   Cold plasma heat - treatment
achieved higher heat efficiency than ordinary
heat - treatment because of a both
complexing heating from inside the sample
by microwave - heating and from surface -
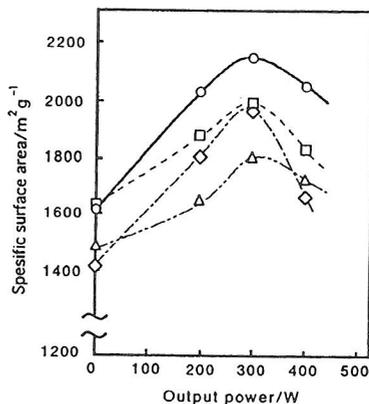heating of the samples by plasma gas

Fig.2 Relationship between specific surface area
and microwave output power:(○)Sample-A,
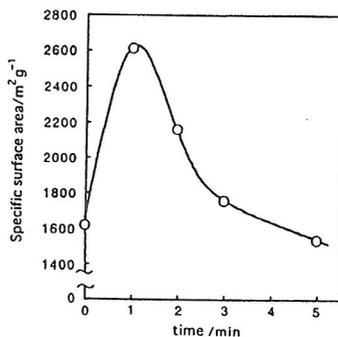(□)Sample-B,(△)Sample-C,(◇)Sample-D.
treatment time;2min

Fig.3 Relationship between specific surface area and
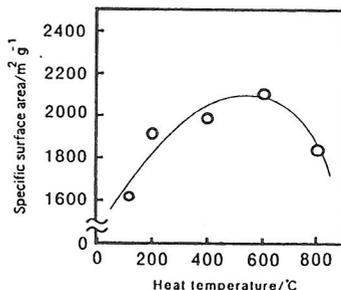plasma heating time:output power;300W,Sample;A

Fig.4 Relatioship between specific surface
area and temperature of evacuation heating:
treatment time;1h, Sample;A

molecules. It can be assumed that because this method has a high heat efficiency and proper temperature for formation of the pores, samples which have a large specific surface can be obtained in a short time.

3.2 Morphological observations by SEM

The morphology of samples prepared by cold plasma heat - treatment, by evacuation heat - treatment and of untreated raw material were observed by SEM. These SEM micrographs are shown in Fig.5. The holes seen in the micrographs are macropore[17]. In the case of untreated raw materials, adhesion of much dusts and particles was observed in and around the macropores. By evacuation heat - treatment, the amount of these dusts and particles was slightly reduced. In the case of samples prepared by plasma heat - treatment, the amount of dust and particles was considerably reduced in and around the macropore and it became apparent that the sample had a tidy surface formation.
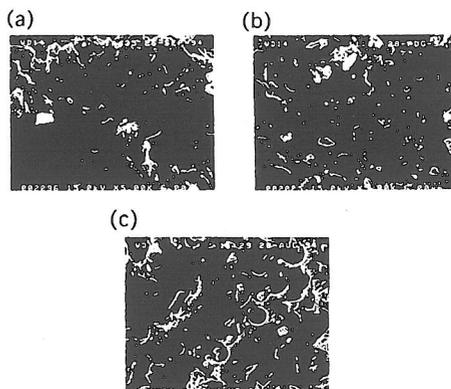
(a)   (b)

(c)

Fig.5 SEM photographs of (a) raw material activated carbon,(b)activated carbon prepared by evacuation heating in an electric furnace and (c) activated carbon prepared by plasma heating.

3.3 Measurement of surface roughness by AFM

Since an AFM has resolving power of about 1nm, it can be assumed that AFM can obtained informations of sub - micropore formations of activated carbons. Surface morphology of the samples prepared by microwave cold plasma heat - treatment and untreated raw materials were observed by AFM. The surface roughness is shown in Table.2. The

Table. 2   Surface roughness of the samples determined by AFM mesurement

Sample	Surface roughness (nm)
raw material	0.11
Plasma heat-treated (300W, 2min)	0.21

Condition of AFM measurement :
Scan area,30nm×30 n m ; Hight scale,
50nm ; Scan rate,1.0Hz

numerical values in the table means that the more this value is increased, rougher the surface of the sample becomes. It was found that the surface of plasma heat - treatment samples has a richer roughness than untreated raw material.

This rich rough surface form by plasma heat - treatment is the considered the main reason for the increased specific surface area of the sample. It could be guessed that this roughness was due to the radical dehydration from the activated carbon.

3.4 Adsorption quantity of various organic substances

The amount of carbon disulfide, benzene, ethyl acetate and toluene adsorbed on the surface of samples prepared by microwave cold plasma and untreated raw material was measured using a gas - phase adsorption measurement apparatus. The results are shown in Table.3. When comparing the amount of organic substance adsorbed per unit of weight, it was clear that by plasma treatment, the amount of adsorption of the sample increased more than that of untreated raw material. This was due to the increase in the specific surface area by plasma heat - treatment.

Comparing the amount of organic substance adsorbed per unit area, the amount of carbon disulfide and benzene adsorbed on the surface of the plasma heat - treatment

samples was much
more than for untreated
raw material. The
fact that the amount of
these organic sub -
stances adsorbed was
increased, suggests that
the surface of the
activated carbon is
improved by plasma
heat - treatment. As

Table 3 Gas phase adsorption amounts of various organic compounds

sample	carbon disulfide		benzene		ethyl acetate		toluene	
	mmol·g^{-1}	μmol·ni^{-2}	mmol·g^{-1}	μmol·ni^{-2}	mmol·g^{-1}	μmol·ni^{-2}	mmol·g^{-1}	μmol·ni^{-2}
raw material[a]	8.50	4.64	1.29	0.70	5.49	3.00	2.27	1.24
plasma heat-treated sample[b]	12.5	5.74	1.87	0.85	6.51	2.98	2.77	1.20

a) Samples were pretreated by evacuation heating at 120°C for 1h in an electric furnace

b) Output power, 300W : treatment time, 2min

carbon disulfide and benzene are non polar organic compounds, it seems one reasons is that polar functional groups such as the carboxyl group on the surface of the sample were removed by the plasma treatment, lowering the polarity of the sample surface.

4. Conclusion

In this study, to investigate the efficiency of microwave cold plasma heat - treatment of activated carbon, the following were conclusion obtained.

(1)The specific surface area of activated carbon could be increased in a short period time by microwave cold plasma heat - treatment.

(2)The microwave cold plasma heat - treatment has a cleaning effect by removing dusts and particles inside the pores of activated carbon.

(3)It has become apparent that the surface of samples prepared by plasma treatment have a very rough form.

(4)The adsorptive properties of activated carbon against various organic substances was improved by microwave cold plasma heat - treatment, especially the adsorptive ability against carbon disulfide was improved.

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