Activation of carbonaceous materials by combined KOH chemical treatment and microwave irradiation

Introduction

Activated carbon (AC)‥ High surface area, Microporous material

Various applications
- Separation, Purification, Drying, Catalyst support
- Gas storage (H_2, CH_4 etc…)
- Electrode for electric double layer capacity
- Adsorption heat pump, Desiccant humidity conditioner

◆ **Pore structure** (Surface area, Pore volume, Pore size)
◆ **Surface characteristics** (Surface functional group)

Be carefully controlled to improve performance

Control factor

Carbonaceous materials	: Phenol resin, Coconut shell, Coke, Plastics …	Many researches
Activation methods	: Chemical activation (KOH, NaOH, H_3PO_4 …)	
	Gas activation (Water vapor, CO_2 …)	
Activation conditions	: Temperature, Heating rate, Amount of activating agent…	
Heating methods	: Electric furnace	

Novel heating method ‥ Microwave heating
- Rapid heating
- Direct heating

In this study

○ Activated carbons were prepared by combined KOH chemical treatment and MW irradiation with various weight ratios of KOH to raw material and MW powers.

○ Pore structure of activated carbon was compared for microwave and electric furnace heating.

○ The applicability of activated carbon to adsorption heat pump (AHP) and desiccant humidity conditioner (DHC) was evaluated based on the effective water adsorptivity for both systems.

Experimental

Procedure

Phenolic resin — Average particle size: 150 μm

KOH — Purity: > 85 %

Ion-exchanged water

Mixing — KOH ratio: R=2, 4, 6 (R=KOH [g]／Phenol resin [g])

Drying — at 353 K for 48 h, Under reduced pressure

Phenolic resin/KOH mixture

Microwave (MW) Heating	Electric Furnace (EF) Heating
MW power, P: 0.26 kW for 450 s, 0.39 kW for 300 s, 0.52 kW for 225 s	Temperature: 773-1073 K KOH ratio: R=4 Holding time: 3600 s (Heating rate: 2 K/min), 0 s (Heating rage: 30 K/min)

Washing — by ion-exchanged water

Drying — at 383 K under reduced pressure

Activated carbon

Apparatus

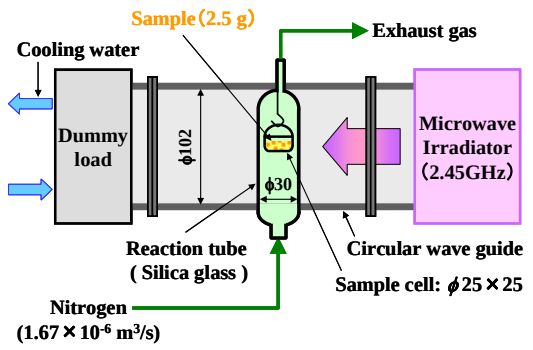


Fig. Schematic diagram of experimental apparatus

Analysis

○ Nitrogen adsorption isotherm
- BET surface area (S_{BET})
- Pore volume: Total (V_{Total}) at p/p_s=0.995; Micro (V_{Micro}) at p/p_s=0.1; Meso (V_{Meso}) by $V_{Total}-V_{Micro}$
- Pore size distribution by BJH method

○ Water vapor adsorption isotherm
- Water adsorptivity
- Effective water adsorptivity in the operation relative pressure ranges of AHP & DHC (Δq_{AHP}, Δq_{DHC})

Results & Discussion

Heating characteristics with microwave irradiation

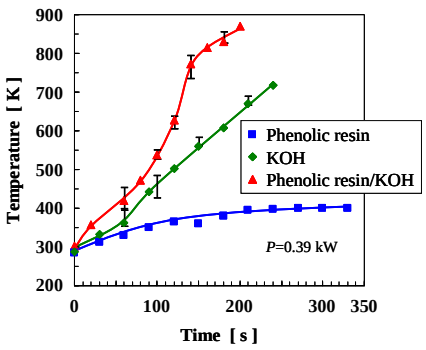


Fig. Temperature profile of samples with microwave heating

■ *Phenolic resin*
Temperature gradually increased with time to attain a constant value of 413 K.

◆ *KOH*
Temperature linearly increased and reached over 700 K.

▲ *Phenolic resin/KOH mixture*

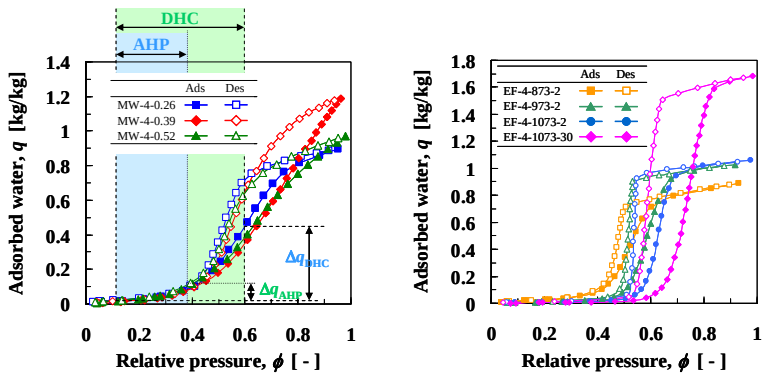
Up to 500-600 K
Temperature rose with a similar trend to that for KOH.

Over 600 K
Temperature rapidly rose over 800 K within 200 s.

Initial period of MW heating (within 100 s)
Phenolic resin/KOH mixture was mainly heated by absorption of MW energy by KOH.

Beyond 100 s
Owing to carbonation and activation of mixture, MW absorptivity of the mixture changed significantly, which brought about a rapid temperature increase.

Water vapor adsorption of ACs prepared



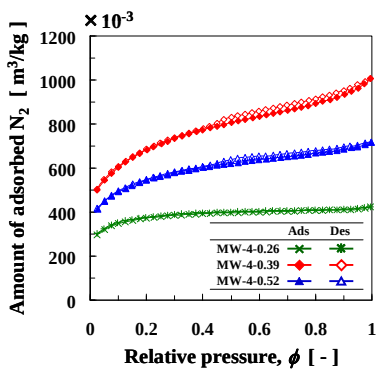
a) Microwave heating　　b) Electric furnace heating

Fig. Water vapor adsorption isotherm of activated carbon

***Microwave heating*: Type III** (BDDT classification)
Amount of adsorbed water gradually and monotonically increased as relative pressure.

***Electric furnace heating*: Type IV**
Adsorption isotherm had almost no adsorption up to around p/p_s=0.4.
A steep increase in uptake was observed at higher relative pressure.
(Most typical shape of water adsorption for AC).

Pore structure of ACs prepared with MW and with EF heating



BJH method

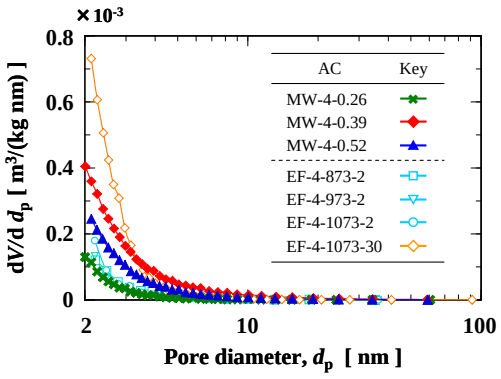


Fig. N_2 adsorption isotherm of ACs by microwave heating　　*Fig.* Pore size distribution of ACs prepared with microwave and with electric furnace heating

Table Pore structure and effective water adsorptivity of ACs prepared

a) Microwave heating

Sample	R [-]	P [kW]	S_{BET} [m²/kg]	V_{Total} [m³/kg]	V_{Meso} [m³/kg]	V_{Meso}/V_{Total} [%]	Δq_{AHP} [kg/kg]	Δq_{DHC} [kg/kg]
			×10³	×10⁻³	×10⁻³			
MW-4-0.26	4	0.26	1129	0.656	0.117	17.8	0.058	0.457
MW-4-0.39	4	0.39	**2208**	**1.559**	0.622	**39.9**	0.085	0.396
MW-4-0.52	4	0.52	1723	1.114	0.351	**31.5**	0.097	0.384
MW-2-0.39	2	0.39	750	0.459	0.084	18.4	0.119	0.325
MW-6-0.39	6	0.39	1362	0.807	0.194	24.0	0.102	0.366

b) Electric furnace heating

Sample	r [K/min]	T [K]	S_{BET} [m²/kg]	V_{Total} [m³/kg]	V_{Meso} [m³/kg]	V_{Meso}/V_{Total} [%]	Δq_{AHP} [kg/kg]	Δq_{DHC} [kg/kg]
			×10³	×10⁻³	×10⁻³			
EF-4-873-2	2	873	1892	1.083	0.257	23.7	0.055	0.691
EF-4-973-2	2	973	2118	1.184	0.268	22.6	0.017	0.582
EF-4-1073-2	2	1073	2279	1.274	0.315	24.7	0.008	0.265
EF-4-1073-30	30	1073	2599	1.465	0.511	**34.9**	0.006	0.049

Microwave heating
MW-4-0.39 : Maximum S_{BET} & V_{Total} of **2,208**×10³ m²/kg & **1.559**×10⁻³ m³/kg.
MW-4-0.39 & MW-4-0.52 : Mesopores accounted for over **30 %** of total pores.
Higher ratio of mesopore than conventional ACs at r=2 K/min.

Electric furnace heating
Heating rate of 2 K/min : Microporosity.
Heating rate of 30 K/min : **Mesopore ratio higher by 10 %** than AC prepared at r=2 K/min.

Rapid heating promoted development of mesopores

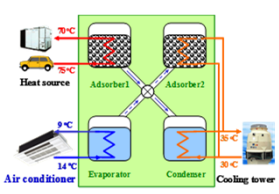
Applicability of AC by microwave heating to AHP & DHC

AHP : Δq_{AHP}-MW_AC ≪ Δq_{AHP}-Silica gel = 0.158 $g_{-H2O}/g_{-silica\ gel}$

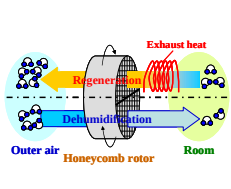
DHC : Δq_{DHC}-MW-4-0.26 = 0.457 g/g > Δq_{DHC}-Silica gel = 0.295 g/g

×1.5

Activated carbons by microwave heating have an applicability to desiccant humidity conditioner



Adsorption heat pump



Desiccant humidity conditioner

Conclusion

- Both phenolic resin/KOH mixture and potassium hydroxide were rapidly heated over 700 K within 240 s, activated carbon was produced from the mixture in a short time.
- For AC prepared at KOH/ phenolic resin weight ratio, R, of 4 and at MW power, P, of 0.39 kW, S_{BET} and V_{Total} reached maximum values of 2,208×10³ m²/kg and 1.559×10⁻³ m³/kg, respectively.
- Activated carbon prepared under microwave heating at P=0.39 and 0.52 kW had high ratio of mesopore to total pore compared to ACs prepared with slow electric furnace heating.
- Activated carbon prepared prepared at R=4 and at P=0.26 kW had 1.5 times higher effective water adsorptivity for desiccant humidity conditioner than a commercial silica gel.

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