Adsorption Characteristics of Harmful Gases on Coke-derived Activated Carbon Prepared by KOH Chemical Activation

Introduction

Petroleum coke・・ Carbon residue produced in oil refining and upgrading processes

- ◎ High carbon content
- ◎ Cheap
- △ High sulfur content
- △ High metal content (Ni, V etc.)

Conventional utilizations of petroleum coke

- Energy/power generation in oil and concrete industries
- Titanium dioxide production
- Carbon and graphite electrodes fabrication for steel and aluminium industries

In the future: the upgrading of heavy oil will increase

⇨ **Production of petroleum coke will increase**

Novel utilization of petroleum coke is required !

In this study: *We have focused on preparation of* ***activated carbon*** *from* ***petroleum coke by KOH chemical activation***

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

Various applications
- Adsorption & concentration of harmful gases
- Separation, Purification, Drying, Catalyst support
- Gas storage (H_2, CH_4 etc.), Energy storage (Electric Double Layer Capacitor)
- Adsorption heat pump, Desiccant humidity conditioner

Adsorption of harmful gases with coke-derived activated carbon

- **Many kinds of harmful gases are produced in oil refinery.**
- **Coke-derived activated carbon can be utilized on site.**

Contents of this study

- Activated carbons were prepared from Orinoco Belt Oil derived petroleum coke under various activation temperatures and KOH/Coke weight ratio. Pore structure and surface chemistry of prepared AC were evaluated.
- Adsorption characteristics of NH_3 gas, which is exhausted from various industries as waste gas, were evaluated for the prepared activated carbon.

Experimental

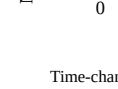
Raw material

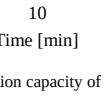
Raw material: **Petroleum coke**
produced from delayed coking unit
in Orinoco Belt in Venezuela
Particle size: **150-212 μm**

Table Chemical composition of petroleum coke [wt%]

C	H	N	S	V	Ni
82.03	3.87	1.91	3-4	0.2	0.05

Procedure

Petroleum coke Particle size: 150-212 μm 

KOH Purity: ＞ 85 % 

Physically Mixing
KOH ratio: *R*= 2, 4, 6
（*R*=KOH [g]／Petroleum coke [g]）

Electric Furnace Heating
Activation temperature : 873, 973, 1073 K
Heating rate : 2 K/min
Holding time : 15 min

Washing by HCl solution and ion-exchanged water

Drying at 393 K under reduced pressure

Activated carbon

Analysis

○ Pore structure

Nitrogen adsorption isotherm by Autosorb-1
- 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
- Pore size distribution by BJH method

○ Surface chemistry

Boehm titration method
- Amount of surface acid functional group

○ NH_3 adsorptivity

Weight change by thermogravimetric analyzer (TG)
- Amount of adsorbed NH_3

Activated carbon

Degassing at 413 K for 24 h under vacuum condition

Setting TG of 5 mg of AC

Degassing at 413 K for 1 h under N_2 flow

Adsorption at ads. temp. of 303-373 K & P_{NH3}=0.1-84 kPa

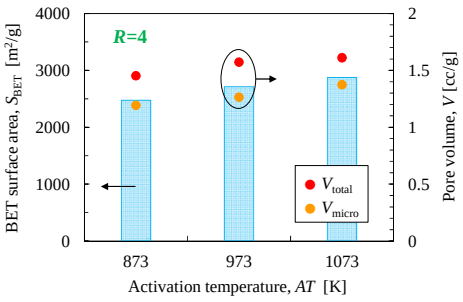
Results & Discussion

Pore structure and Surface chemistry of ACs prepared

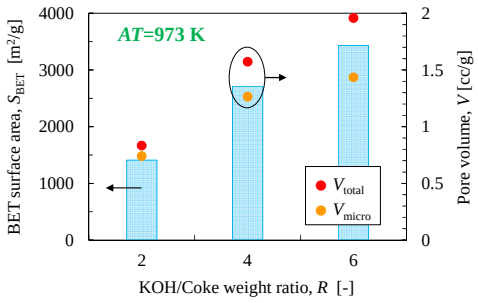
Table Pore structure of coke-derived activated carbons

	AT=873 K		*AT*=973 K		*AT*=1,073 K	
	S_{BET} [m²/g]	V_{total} [cc/g] V_{micro} [cc/g]	S_{BET} [m²/g]	V_{total} [cc/g] V_{micro} [cc/g]	S_{BET} [m²/g]	V_{total} [cc/g] V_{micro} [cc/g]
R=2	1,204	0.73 0.62	1,409	0.83 0.74	1,471	0.86 0.77
R=4	2,473	1.45 1.19	2,746	1.57 1.26	2,875	1.61 1.37
R=6	2,197	1.30 1.05	3,431	1.96 1.44	3,950	2.14 1.49

～ *Effect of activation temp. on pore structure* ～



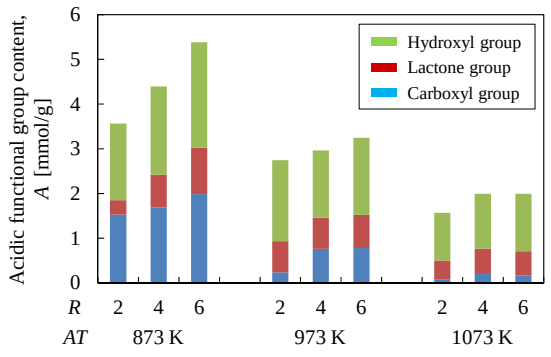
～ *Effect of KOH/Coke ratio on pore structure* ～



As increasing activation temperature and KOH/Coke weight ratio,

- **BET surface area, micro and total pore volume increased**
- **Volume ratio of mesopore/total pore increased**

～ *Amount of Surface acidic functional groups of AC* ～



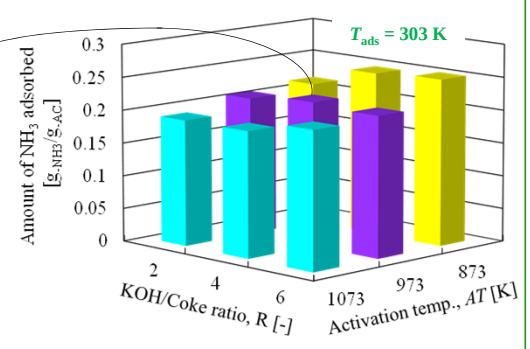
Amount of hydroxyl, lactone and carboxyl groups of coke-derived ACs

- **Higher activation temperature, Lower functional groups content**
- **Higher KOH/Coke weight ratio, Higher functional groups content**
- **Hydroxyl functional group is over 40 % of the total functional groups**

Adsorption characteristics of ammonia gas on ACs prepared

～ *NH_3 adsorption capacity of ACs prepared* ～

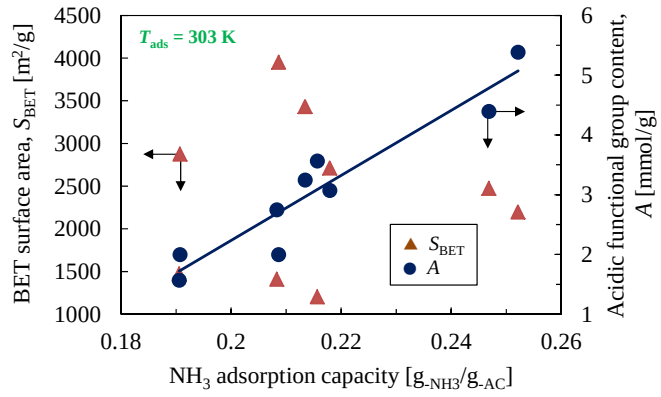
Time-change in NH_3 adsorption capacity of prepared AC at adsorption temperatures of 303, 333 and 363 K



NH_3 adsorption capacity at 303 K in an equilibrium state of AC prepared at various *AT*s and *R*s

- **Ammonia adsorption on AC proceeded quickly, and attained in an adsorption equilibrium within 3 min.**
- **As increasing adsorption temperature, NH_3 adsorption capacity drastically decreased.**
  ⇨ **Physisorption may be playing a key role in this case.**
- **Higher activation temperature, Lower NH_3 adsorption capacity**
- **Higher KOH/Coke weight ratio, Higher NH_3 adsorption capacity**

～ *Effect of S_{BET} and A on NH_3 adsorption capacity at 303 K* ～



Relationship between surface area, functional group content and NH_3 adsorption capacity

- **A linear relationship was observed between NH_3 adsorption capacity and functional group content.**
  ⇨ **Surface acidic functional groups play an important role to NH_3 adsorption on AC even at 303 K.**

Conclusion

- Activated carbon with high surface area over 3,000 m²/g was produced from Orinoco Belt Oil derived petroleum coke in Venezuela.
- Development of pore structure was promoted when petroleum coke was activated with KOH at higher activation temperature and KOH/Coke weight ratio.
- Surface acidic functional group content and NH_3 adsorption capacity of AC at 303 K increased as decreasing in activation temperature & increasing in KOH/Coke weight ratio.
- A linear relationship was observed between NH_3 adsorption capacity and functional group content at adsorption temperature of 303 K.

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