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

Conventional utilizations of petroleum coke
  ◆ Energy-power generation in oil and related industries
  ◆ Titanium dioxide production
  ◆ Carbon and graphit electrode fabrication for steel and aluminum industries

In the future: the upgrading of heavy oil will increase
  Production of petroleum coke will increase

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
  ◆ Coke derived activated carbon can be utilized on site.
  ◆ Many kinds of harmful gases are produced in oil refinery.
  ◆ Coke derived activated carbon was promoted when petroleum coke was activated with KOH at higher activation temperature and KOH/Coke weight ratio.

Activated carbon 

Activated carbon were prepared from Orinoco Belt Oil derived petroleum coke under various activation temperatures.

Effect of activation temp. on pore structure

In this study:

Activated carbon
In the future:
the upgrading of heavy oil will increase

Activated carbon with high surface area over 3,000 m²/g was produced from Orinoco Belt Oil derived petroleum coke in Venezuela.

Adsorption characteristics of coke-derived activated carbon

Effect of KOH/Coke ratio on pore structure

Pore structure and Surface chemistry of prepared AC were evaluated.

Activated carbon
Prepared activated carbon.

Activated carbon

Activated carbon from coke derived ACs

Adsorption characteristics of harmful gases with coke-derived activated carbon

Many kinds of harmful gases are produced in oil refinery.

Adsorption of harmful gases by KOH

Acidic functional group content,

BET [m²/g]

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

Effect of KOH/Coke ratio on pore structure

~ 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

As increasing activation temperature, BET/Coke weight ratio increased

~ Amount of Surface acidic functional groups of AC ~

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

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 NH3 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 NH3 adsorption capacity and functional group content at adsorption temperature of 303 K.

Experimental

Raw material: Petroleum coke 
produced from delayed coking unit in Orinoco Belt in Venezuela

Table: Chemical composition of petroleum coke [wt%]

<table>
<thead>
<tr>
<th>C</th>
<th>H</th>
<th>N</th>
<th>S</th>
<th>V</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>82.01</td>
<td>3.87</td>
<td>1.91</td>
<td>3.4</td>
<td>0.2</td>
<td>0.05</td>
</tr>
</tbody>
</table>

Petroleum coke

Particle size: 150-212 μm

KOH Purify > 95 %

Procedure

Physical Mixing

KOH ratio: 2, 4, 6

4\(\text{g KOH/g Petroleum coke}\)

Electric Furnace Heating

Activation temperature: 873, 973, 1073 K

Heating rate: 2 K/min

Holding time: 15 min

Washing

by 10% solution and is-exchanged water

Drying

at 393 K under reduced pressure

Degasing

at 413 K for 24 h under vacuum conditions

Setting

TG at 5 °C of AC

Degasing

at 413 K for 1 h under N2 flow

Adsorption

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

Analysis

Table: Chemical composition of coke derived AC [wt%]

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<tr>
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Petroleum coke

Particle size: 150-212 μm

KOH Purify > 95 %

NH3 adsorption capacity drastically decreased.

Lower NH3 adsorption capacity

Higher KOH/Coke weight ratio,
Higher NH3 adsorption capacity

Ammonia adsorption on AC proceeded quickly, and attained in an adsorption equilibrium within 3 min.

NH3 adsorption capacity of AC

NH3 adsorption capacity at 303 K in quench samples of AC prepared at various KOH ratios

As increasing adsorption temperature, NH3 adsorption capacity drastically decreased.

Physiosorption may be playing a key role in this case.

Results & Discussion

Table: Pore structure of coke-derived activated carbons

<table>
<thead>
<tr>
<th>Condition</th>
<th>(SBET) [m²/g]</th>
<th>(V_m) [cc/g]</th>
<th>(V_t) [cc/g]</th>
<th>(S_H) [m²/g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>(R=2)</td>
<td>1.09</td>
<td>1.08</td>
<td>1.05</td>
<td>1.03</td>
</tr>
<tr>
<td>(R=4)</td>
<td>1.45</td>
<td>1.53</td>
<td>1.57</td>
<td>1.44</td>
</tr>
<tr>
<td>(R=6)</td>
<td>1.45</td>
<td>1.47</td>
<td>1.61</td>
<td>1.49</td>
</tr>
</tbody>
</table>

Time-change in NH3 adsorption capacity of prepared AC

0.05
0.1
0.15
0.2
0.25
0.3
0.35
0.4
0.45
0.5
0.55

Time [min]

Amount of NH3 adsorbed

0
0.1
0.2
0.3
0.4
0.5

\(T=303\ K\)

\(T=373\ K\)

\(T=403\ K\)

\(T=433\ K\)

\(T=463\ K\)

\(T=493\ K\)

NH3 adsorption capacity of AC prepared at various KOH contents

Higher activation temperature,
Higher KOH/Coke weight ratio,
Higher NH3 adsorption capacity

NH3 adsorption capacity at 303 K in quench samples of AC prepared at various KOH contents

NH3 adsorption capacity at 303 K

Higher activation temperature,
Lower NH3 adsorption capacity

NH3 adsorption capacity at 303 K

Higher KOH/Coke weight ratio,
Higher NH3 adsorption capacity

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NH3 adsorption capacity of AC

NH3 adsorption capacity at 303 K in quench samples of AC prepared at various KOH ratios

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Physiosorption may be playing a key role in this case.

~ Effect of \(S_{BET}\) and \(A\) on NH3 adsorption capacity at 303 K ~

A linear relationship was observed between NH3 adsorption capacity and functional group content.

Surface acidic functional groups play an important role to NH3 adsorption on AC at even 303 K.

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