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Preparation of Sulfur-contained Activated Carbon from Petroleum Coke

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High sulfur petroleum coke (HSPC, 7.6 wt-S%) was employed to prepare activated carbons (ACs) using KOH to develop pore structure with remaining sulfur content for supplying post oxidation treatments to effectively generate sulfo groups which could be a stronger adsorption sites of cationic heavy metal ions in aqueous solutions than carboxy groups. KOH activation was conducted at 550–800 °C by two methods of physical mixing (KOH and HSPC solid-solid mechanical mixture) and impregnation (KOH solution and HSPC liquid-solid mixture and then dried in oven). Prepared samples were characterized with nitrogen adsorption-desorption isotherms and elemental analysis. Physical mixing was effective for HSPC of large particle size, whereas impregnation was effective for small particle. Based on the experimental results, mild activation conditions such as KOH/HSPC ratio of 1 and temperature of 550 °C were preferable; specific surface areas and remaining sulfur contents of the resultant ACs by physical mixing and impregnation methods could be achieved 651 m²/g, 2.9 wt-S% and 812 m²/g, 5.2 wt-S%, respectively. Post oxidation of the ACs and the consecutive Ni(II) adsorption experiments implied that sulfo groups that could work even in acidic region might be generated on ACs from HSPC comparing with ACs from low sulfur petroleum coke.

Keywords

Sulfur, Potassium hydroxide activation, Pore structure, Petroleum coke, Activated carbon

1. Introduction

Petroleum coke (PC) is by-product of petroleum industry and composed primarily of carbon. Low sulfur petroleum coke (LSPC) is used as fuel and carbonaceous material^{1),2)}. The use of high sulfur petroleum coke (HSPC) has some problems, excess amounts of SO_x will be generated in combustion and other oxidation treatments for instance, thus they were rarely used^{3),4)}. Thereby some new applications for HSPC have been required and then preparation of activated carbons (ACs) from HSPC was examined in the present study. Activated carbon is a porous material, and is recognized to be useful as adsorbents, catalysts and capacitors^{5)~7)}. In recent years, several studies reported that activated carbons (ACs) containing sulfur showed more excellent performance than ACs without sulfur when used as electrodes, catalysts and capacitors^{8)~10)}.

Zhang *et al.*³⁾ prepared AC for natural gas adsorbents from HSPC (4.8 wt% of sulfur) by KOH activation.

Pore developments were observed for the resultant materials, although they contained only a low amount of sulfur. In our previous study, similar results were observed¹¹⁾. HSPC (7.6 wt%) based activated carbon (2120 m²/g) was prepared by KOH activation (PC/KOH mass ratio: 3, activated temperature: 800 °C), and the result showed that sulfur content was significantly reduced (0.15 wt%). These findings suggested that conventional activation methods could not develop porous structure of HSPC with keeping the high sulfur content.

In our preliminary study, AC containing a small amount of sulfo group could be prepared from HSPC. From the results, two steps were required for the preparation; (1) sulfur-containing AC was prepared from HSPC, and (2) sulfur species remained on the surface of prepared AC were converted to sulfo group by oxidation treatment. In this study, KOH activation conditions to achieve first step were mainly examined to obtain porous and high sulfur carbon materials. Post oxidation treatments of the prepared ACs and adsorption performance of Ni(II) ion were also investigated as a trial.

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2. Materials and Methods

2.1. Raw Materials

High sulfur (7.6 wt%) PC (HSPC, delayed coke) was employed as raw material in this study. HSPC was grained and sieved to 1, 5, 10, 30, 150 and 710 (average of 420-1000) μm . Raw materials were labeled as PC(X), in which X in parenthesis stood for particle size in μm . Low sulfur (0.52 wt%) PC (LSPC, green coke) was also supplied as a reference.

2.2. KOH Activation

2.2.1. Physical Mixing Method

HSPC was physically mixed with potassium hydroxide solid (KOH and HSPC solid-solid mechanical mixture) at various KOH/PC mass ratios (R) of 1, 2 and 3. The mixture was heated in a horizontal tube furnace from room temperature up to a set values (550 °C or above) at 10 °C/min under N_2 gas flow by 100 mL/min. After keeping the sample for 0.0-0.5 h at the set temperature, the furnace was cooled down to room temperature. The sample was washed with 1.0 M HCl and then hot distilled water repeatedly until solution pH was no longer changed and dried overnight at 110 °C in the final step. The prepared sample was labeled as PC(X)-KA_B_C, where A is the KOH/PC mass ratio (R), B is the activation temperature [°C] and C is holding time [h].

2.2.2. Impregnation Method

HSPC and potassium hydroxide aqueous solution were mixed and stirred for 1.5 h. Then, the mixed slurry was dried overnight at 110 °C. The subsequent activation methods were the same as those described for physical mixing methods. The prepared sample was labeled as PC(X)-Kaqa_B_C.

2.3. Sample Oxidation

Oxidation was conducted using prepared ACs derived from HSPC and LSPC with PC(710)-K1_550_0.5 as an activation method. The prepared AC (0.5 g) was soaked in 30 mL mixed solution (30 % H_2O_2 (10, 7.5, 6 mL) and 13.6 mol/L HNO_3 (20, 22.5, 24 mL)) and stirred in a constant temperature bath ranging 30-60 °C for 6 h or 24 h. After oxidation, the sample was washed with hot distilled water repeatedly, and then dried overnight at 110 °C. The prepared sample was appended (1 : x)_y_z, where x is the H_2O_2 : HNO_3 volume ratio, y is the oxidation temperature [°C] and z is oxidation time [h].

2.4. Adsorption Experiment

Adsorption experiment of Ni(II) in aqueous solution was performed in a batch system. Each sample was dried at 110 °C for 30 min before use. Ni(II) solution of 1000 mg/L was prepared by dissolving $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in distilled water and the initial concentration was adjusted. A 40 mg of the sample was added to 5 mL of the Ni(II) solution in 30 mL Erlenmeyer flask and stirred at 100 rpm for 24 h at 25 °C. Initial solution

pH (pH_0) was adjusted to 1.5-2.0 with HNO_3 solutions in order to investigate the effect of sulfo group. The Ni(II) concentrations of the solutions before and after adsorption were determined by atomic absorption spectrometer (novAA 300, Analytik Jena AG).

2.5. Sample Characterization

Pore properties of the samples were characterized by the N_2 adsorption-desorption isotherms at -196 °C with a specific surface area and pore size distribution analyzer (BEL SORP-mini II, MicrotracBEL Corp.) for ACs prepared from HSPC. The sample was degassed at 300 °C for 1 h under vacuum condition prior to analysis. The specific surface area (S_{BET} , m^2/g) was obtained using the Brunauer-Emmett-Teller (BET) method¹²⁾. The total pore volume (V_{total} , cm^3/g) was estimated by the quantity of gas adsorbed at a P/P_0 of 0.995. The micropore volume (V_{micro} , cm^3/g) was determined by the α_s -plot with subtracting pore effect (SPE) method¹³⁾. The mesopore volume (V_{meso} , cm^3/g) was calculated by the difference between V_{total} and V_{micro} . The average pore diameter (D_{ave} , nm) was estimated assuming slit shaped pore.

Elemental composition (wt%) for each sample was also examined. The contents of carbon (C), hydrogen (H) and nitrogen (N) were measured in accordance with JIS M 8813. Sulfur (S) content was determined by LECO method (JIS M 8819). Elements other than C, H, N and S were assumed to be oxygen (O), and O content was calculated by the difference.

The X-ray photoelectron spectroscopy (XPS) analysis was carried out with PHI 1800 (ULVAC-PHI, Inc.). An analytical sample was prepared by compacting the sample on the Cu tape. A constant analyzer pass energy of $E_p = 23.5$ eV and the monochromatized Al $K\alpha$ line were used in all XPS measurements.

3. Results and Discussion

3.1. Effect of Particle Size

Figure 1 shows the relationship between S_{BET} and particle size. In physical mixing method, S_{BET} of activated carbon increased from 202 to 1019 m^2/g in proportion to the particle size of precursor from 10 to 710 μm . Since pulverized petroleum cokes (PCs) did not contact with melted KOH completely during activation, pore development of PCs did not progress very well.

On the other hand, in the impregnation method, S_{BET} of prepared sample expanded from 1002 into 1502 m^2/g in proportion to the particle size of precursor from 1 to 10 μm . Then, S_{BET} decreased to 629 m^2/g , while particle size of cokes enlarged up to 150 μm . The impregnation method seemed to work well toward solution to penetrate PC (AC precursor) easily. However, the solution was hard to soak deep into PC. Therefore, in the impregnation method, KOH activation was pro-

gressed by the reaction only with KOH adhering to the precursor surface. Small particle size petroleum coke was covered more with KOH, thus S_{BET} of activated carbon prepared by impregnation method increased as the decreased of the particle size. However, in the range of particle size smaller than 10 μm , S_{BET} decreased, because insufficient mixing with KOH solution, some of the PC powder was floating even after mixing KOH solution and PC, should result in poor dispersion of KOH onto the PC surface before the heating for activation.

3. 2. Effect of Activation Temperature and KOH Amount

Figure 2 shows the activation results when activation temperature was changed to 550 $^{\circ}\text{C}$ and 800 $^{\circ}\text{C}$ with the KOH/PC mass ratio of 1.0. In the physical mixing method, when activation temperature was raised from

Fig. 1 Relationship between the Surface Area of the Prepared Samples and the Particle Sizes of Precursors (holding time; 0 h at 800 $^{\circ}\text{C}$)

Fig. 2 Effect of Activation Temperature on (a) Surface Area and (b) Sulfur Content (KOH/PC mass ratio; 1.0, holding time; 0.5 h at 550 $^{\circ}\text{C}$, 0 h at 800 $^{\circ}\text{C}$)

550 to 800 $^{\circ}\text{C}$, S_{BET} of activated PC(710) and PC(150) enlarged from 651 to 1019 m²/g and 654 to 818 m²/g, respectively. On the other hand, sulfur contents reduced from 2.9 to 1.6 wt% and 2.9 to 0.8 wt%, respectively. The same trend was observed for the impregnation method, although sulfur was remained as much as 11.8 wt% in maximum in case of employing polythiophene as an AC precursor¹⁴). When activation temperature was elevated, S_{BET} and sulfur content of activated PC(10) changed from 812 to 1502 m²/g and 5.2 to 0.2 wt%, respectively. It also revealed that pore development was more pronounced by KOH activation at higher temperature. Lee and Choi reported that sulfur contents of PC after NaOH activation at 500 $^{\circ}\text{C}$ and 550 $^{\circ}\text{C}$ were 4.85 wt% and 0.031 wt%, respectively¹⁵). Zhang *et al.* showed that sulfur was not released as sulfur dioxide in KOH activation at 350-550 $^{\circ}\text{C}$ ³). These findings implied that desulfurization reactions of PC might be progressed by KOH activation at higher than 550 $^{\circ}\text{C}$, and desulfurization proceeded as follows:¹⁶⁾

Fig. 3 Effect of KOH/PC Mass Ratio on (a) Surface Area and (b) Sulfur Content (activation temperature; 550 °C, holding time; 0.5 h)

In mild condition such as 500-550 °C, the advance of desulfurization reaction was not enough. Accordingly, it is suggested that activation temperature is one of the important factors to prepare sulfur-remained activated carbon (AC).

KOH activation was carried out at 550 °C with changing the KOH/PC mass ratio, and the results were portrayed in **Fig. 3**. In the physical mixing method, when the KOH/PC mass ratio was increased from 1 to 3, S_{BET} of activated PC(710) and PC(150) expanded from 651 to 2515 m²/g and 654 to 2082 m²/g, respectively. On the contrary, in the impregnation method, almost same S_{BET} (812 m²/g and 878 m²/g) was observed when KOH/PC mass ratio was increased from 1 to 2. In the physical mixing method, melted KOH worked to react with PC completely. Alternatively, KOH could not get into deep inside of PC effectively in impregnation method, then additional KOH more than the ratio of 1 seemed to be actually removed before heating in the experimental procedure; therefore, the addition of KOH could not affect significant impact on pore development. The differences of the effect of KOH addition between those two methods were due to the amount of KOH reacted with PC surface. Furthermore, the sulfur content reduced with increasing the amount of KOH used. Since KOH activation was improved by the large amount of KOH, desulfurization reaction also proceeded. Based on these results, it is necessary to moderate the activation conditions of PC such as activation temperature and KOH amount in order to prepare sulfur-contained AC.

3.3. Effect of Oxidation Treatment

Low sulfur containing activated carbon (LSAC, 678 m²/g, 0.2 wt%) was also prepared from low sulfur petroleum coke (LSPC), and LSAC was used for a reference. **Figure 4** shows the Ni(II) adsorption results on oxidized PC(710)-K1_550_0.5 (HSAC) and LSAC. HSAC tended to exhibit higher Ni(II) adsorption amount than LSAC for 4 samples in total 6 samples at pH 1.5-2.0. This result suggested that Ni(II) adsorption could occur on sulfo group. In case of higher Ni(II) adsorption amounts at LSAC than those at HSAC, sulfo group might be highly integrated for LSAC compared to HSAC. **Table 1** shows the total sulfur and the content of other elements measured by elemental analysis and sulfur species contents of carbon surface calculated by XPS measurement. After oxidation, thiophene was greatly decreased revealing that thiophene species was directly converted to SO₂ during oxidation treatment. Sulfate was also decreased after oxidation. However, most of sulfate on HSAC should be not sulfo group but sulfate salt. Although relatively larger amount of sulfate measured on non-oxidized HSAC than oxidized HSAC could not be explained clearly for the present, Shan *et al.* reported similar observation in KOH activation of high sulfur petroleum

coke¹⁶⁾. Thus, thiophene was partly converted to sulfate (sulfo group) by oxidation treatment. Sulfate remaining after oxidation of HSAC could be attributed to sulfo group from the Ni(II) adsorption amount.

4. Conclusion

In this study, KOH activation conditions were examined to prepare activated carbon (AC) containing sulfur from high sulfur petroleum coke (HSPC). KOH activation was carried out with physical mixing method and impregnation method. The physical mixing was effective for pore development of precursor with large particle size, whereas the impregnation method was suitable for precursor with small particle size and the optimal particle size was 10 µm. Activation temperature and KOH amount are the important factors to prepare sulfur-remained AC. In the activation temperature of 550 °C and KOH/PC mass ratio of 1, HSPC with particle size of 420-1000 µm and 10 µm was activated by physical mixing method and impregnation method, respectively, and surface area and sulfur content of the resultant activated carbons (ACs) were 651 m²/g, 2.9 wt% and 812 m²/g, 5.2 wt%, respectively. A part of remaining sulfur on the HSAC might be converted to sulfo group by oxidation.

Fig. 4 Ni(II) Adsorption Amount of Oxidized PC(710)-K1_550_0.5 (HSAC) and LSAC at pH 1.5-2.0

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Table 1 Sulfur Content and Sulfur Species Amount of Carbon Surface

Sample	Carbon [wt%]	Hydrogen [wt%]	Nitrogen [wt%]	Oxygen [wt%]	Sulfur [wt%]	Thiophene [mmol/g]	Sulfite [mmol/g]	Sulfate [mmol/g]
HSAC	84.7	1.3	0.7	11.0	2.9	0.18	0.13	0.29
HSAC-(1 : 4)-30-24	64.3	1.1	1.7	31.3	1.6	0.03	0.00	0.06
HSAC-(1 : 4)-60-6	71.0	1.1	1.1	24.7	1.2	0.04	0.03	0.14

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要 旨

低質硫黄コークスを利用した硫黄含有活性炭の賦活条件の検討

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硫黄分 (7.6 wt%) を含む石油コークスを原料とし、硫黄分の減少を抑制しながら細孔構造を発達させる KOH 賦活条件の検討を行った。KOH 賦活は物理混合法および含浸法を用いた。物理混合法と含浸法はそれぞれ大粒径および小粒径の原料の細孔発達に効果的であった。KOH / コークスの質量比と賦活温度が上昇すると、比表面積は増加するが硫黄含有率は減少した。したがって、硫黄分の減少を抑制し細孔構造を発達させるためには低温かつ水酸化カリウム量を減らした温和な KOH 賦

活条件が適する。粒径420 ~ 1000 μm の原料を物理混合法にて、また粒径10 μm の原料を含浸法にて、賦活温度550 $^{\circ}\text{C}$, KOH / コークスの質量比1の条件で賦活をした結果、得られた活性炭の比表面積および硫黄含有率はそれぞれ651 m^2/g , 2.9 wt% および812 m^2/g , 5.2 wt% であった。物理混合法で調製した活性炭を酸化処理して Ni(II) イオン吸着を調べたところ、硫黄含有活性炭表面に酸性域でも吸着に有効なスルホ基が生成している可能性が示唆された。

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