SOLVENT WASHING EFFECTS ON THE ADSORPTION AND SURFACE PROPERTIES OF METAL TREATED ACTIVATED CARBONS

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Introduction

Activated carbons have been widely employed for the purification of toxic wastes. To change the adsorption properties of activated carbon, chemical modification has been applied. Supported metal catalyst has been an example of modification of activated carbon. To prepare supported metal catalysts, metallic ions have been either adsorbed or impregnated on activated carbons. It has been known that metal treated activated carbons are excellent materials for the adsorption of toxic species such as hydrocarbons, halogenated hydrocarbons, alcohols, phosgene, hydrogen cyanide, and other materials [1]. Although many studies on the physicochemical properties of the non-treated active carbon have been performed, few studies on the properties of the metal treated carbon have been reported [2,3,4,5]. Therefore, the physical view of the metal treated carbon has not been clearly revealed. Especially, the effects of some parameters such as heat treatment or solvent washing on the physicochemical properties of metal treated activated carbons have not been clearly revealed

In this study, metal treated activated carbons are prepared with various metals such as Ag, Cd, and Cu. The changes in physicochemical properties of metal treated activated carbons are investigated before and after the solvent washing with acetone or ethanol. In order to investigate the physicochemical properties, adsorption isotherms and surface area are obtained. Surface morphologies are investigated by scanning electron microscopy (SEM) to explain the changes in adsorption properties.

Experimental

The activated carbon used as a starting material was prepared from coconut shell based granular type. The carbonized coconut shell was heated first at 500 for burn off, then physically activated with water vapor at the temperature range 750 780 . $AgNO_3$ (Aldrich, 99+ %, ACS reagent) was used as a silver source for Ag treatment, while $CdCl_2$ and $CuCl_2$ (Aldrich, 99+ %, ACS reagent) were used as Cd and Cu sources, respectively. Mole concentrations of of $AgNO_3$, $CdCl_2$ and $CuCl_2$ were 0.1 and 0.8. In order to be free from impurities, doubly distilled water was used to dissolve the chemicals. For the treatment, 30 g of activated carbons were dipped into 100 ml of each metal dissolved aqueous solution and stirred for 24 h at room temperature. Then, air and bubbles in the solutions were removed under the pressure of about 1.33 Pa for 20 min, and then discarded the solution. Finally, these samples were dried at 110 for 48 h in air atmosphere. For the study of solvent washing effects, acetone (Aldrich, 99+ %, ACS reagent) and ethanol (Aldrich, 99+ %, ACS reagent) were used without further purification. Metal treated samples were soaked in a solvent and stirred for 24 hrs. Then, solvent washed samples were dried completely in the oven.

Nitrogen adsorption isotherms at 77 K measured on the Digisorb 2500(Micrometrics Instruments Co., USA) volumetric adsorption analyzer, were used to characterize the porous structure of metal treated activated carbons. BET specific surface area, pore volumes, and pore size distributions for the samples were obtained from nitrogen adsorption isotherms. Scanning electron microscopy (SEM, Topcon sm-300, Japan) was used to observe the surface state and structure of metal treated activated carbons

Results and Discussion

Fig. 1 shows nitrogen adsorption isotherms of metal treated activated carbons after the samples are washed with acetone. From all of the acetone washed metal treated activated carbons, type I isotherms are obtained [6]. Although nitrogen adsorption isotherms of non-washed samples are not shown here, it is recognized that the adsorbed volume of N_2 decreases after the metal treated activated carbons are washed with acetone. Cd treated and Cu treated activated carbons shows significant reduction of adsorbed volume, while Ag treated samples shows less significant reduction. When the amounts of metal treated on the activated carbons are low (treated with 0.1 mole of metal solution), the value of the adsorbed volume of nitrogen is decreased in the order of Ag, Cd, and Cu treated sample after the samples are washed with acetone. When the amounts of metal treated on the activated carbons are relatively high (treated with 0.8 mole of metal solution), the value is decreased in the order of Cd, Ag, and Cu treated sample. These phenomena are probably due to the interaction between acetone and metals treated on activated carbons. The interaction may change metal's physicochemical properties such as oxidation state, shape, and size of particles. Fig. 2 shows nitrogen adsorption isotherms of metal treated activated carbons after the

samples are washed with ethanol. Although nitrogen adsorption isotherms of non-washed samples are not shown here, it is recognized that the adsorbed volume of N_2 decreases after the metal treated activated carbons are washed with ethanol. When the amounts of metal treated on the activated carbons are low (treated with 0.1 mole of metal solution), the value of the adsorbed volume of nitrogen is decreased in the order of Ag, Cu, and Cd treated sample after the samples are washed with ethanol. When the amounts of metal treated on the activated carbons are relatively high (treated with 0.8 mole of metal solution), the value is decreased in the order of Cu, Cd, and Ag treated sample. As a conclusion, it is recognized that ethanol washed samples show different behavior in adsorbed volume from the samples washed with acetone. From these results, it can be postulated that the changes in physicochemical properties of metals treated on activated carbons depend on the solvents employed. Similar results are obtained from the BET surface areas data shown in Table 1. To reveal the causes of the differences in adsorption capacity and specific surface area after the samples are washed with solvents, surface morphology and pore structure of the metal treated activated carbons are investigated by scanning electron microscopy. Fig. 3 shows the surface morphologies of the Cd treated activated carbons before and after the solvent wash. Highly developed porous structure of activated carbon and the distribution of metals are clearly seen. It is also observed that lot of micropores are blocked by metals. Before the samples are washed with solvents, most of the particles are smaller than 2.5 μm in size when the mole concentration is lower than 0.2. Since the size of particle is smaller than cavity size, several particles are observed in a cavity. As the concentration becomes higher, the shape is like dendrite or frostwork. After the Cd treated samples are washed with solvents, dendrite or frostwork shape of Cd particles changed to spherical shape. And the particles are aggregating to form greater size. It is postulated that differences in adsorption properties before and after the solvent wash are mainly due to different blocking effects. And the effects depend on the way of distribution, shape of metal particles, and the pattern of aggregates.

Conclusion

From the studies of nitrogen adsorption isotherms of metal treated activated carbons before and after the samples are washed with acetone of ethanol, the changes in physicochemical properties of metals treated on activated carbons are recognized probably due to interaction between solvents and metals. It is also recognized that ethanol washed samples show different behavior in adsorbed volume from the samples washed with acetone. From these results, it can be postulated that the changes in physicochemical properties of metals treated on activated carbons depend on the solvents employed. Similar results are obtained from the BET surface areas data. From SEM study, it is observed that the shape and size of metal particles are changed after the samples are washed with solvents. Due to these change, different blocking effects will be caused. It is postulated that differences in adsorption properties before and after the solvent wash are mainly due to different blocking effects.

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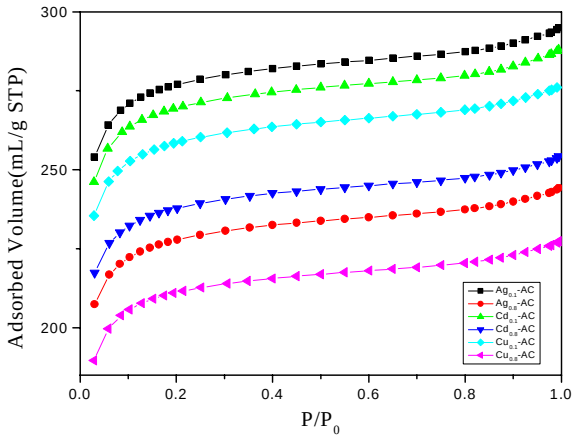

Fig. 1 Nitrogen adsorption isotherms of the acetone washed metal treated activated carbons at 77.3 K.

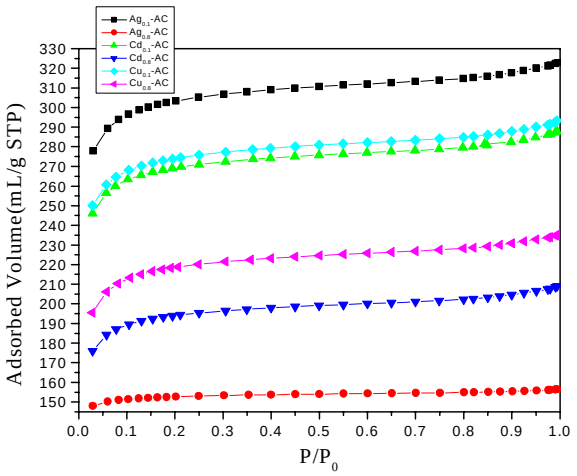

Fig. 2. Nitrogen adsorption isotherms of the ethanol washed metal treated activated carbons at 77.3 K

Table 1. Comparison of BET specific surface area (m^2/g) for the solvent washed metal treated activated carbon

Sample	Non	Acetone	Ethanol
Ag0.1-AC	1122.1	1020.6	931.93
Ag0.8-AC	1062.0	877.32	767.11
Cd0.1-AC	1418.0	898.72	895.90
Cd0.8-AC	1196.8	648.40	631.73
Cu0.1-AC	1361.3	915.20	862.17
Cu0.8-AC	1212.5	734.34	702.98

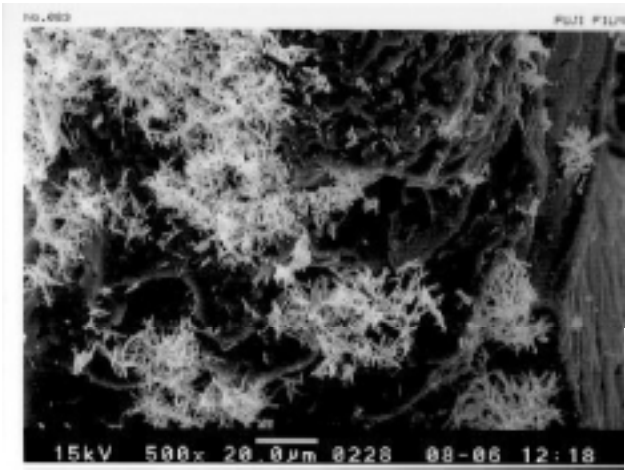

Fig. 3 a) .SEM photographs of the Cd treated (0.1 mole) activated carbons before solvent washing.

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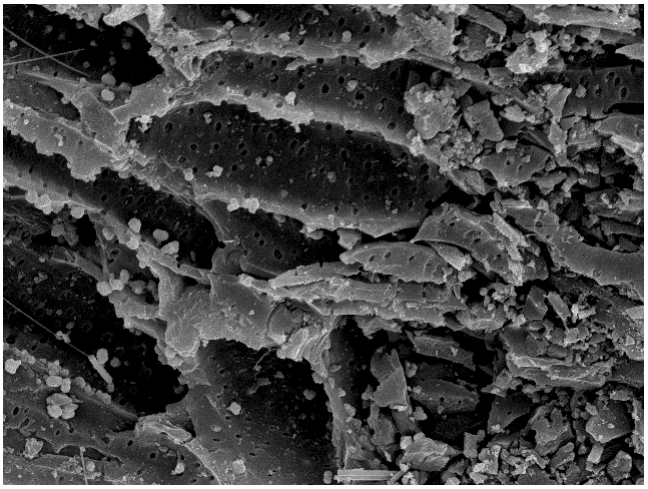

Fig. 3 b) .SEM photographs of the Cd treated (0.1 mole) activated carbons after the samples are washed with acetone..

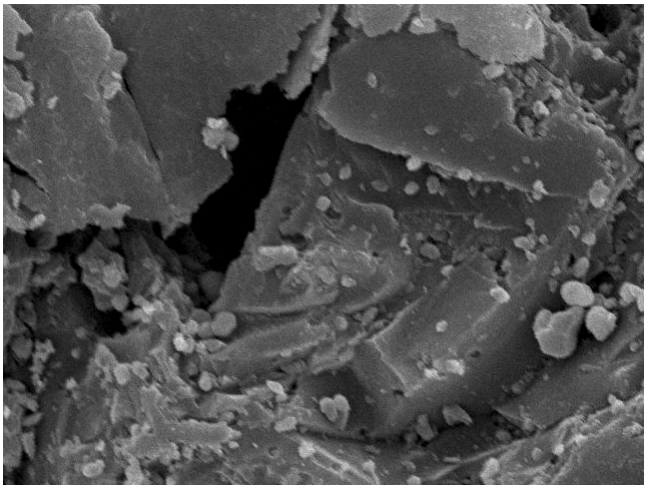

Fig. 3 c) .SEM photographs of the Cd treated (0.1 mole) activated carbons after the samples are washed with ethanol.