Toxic Gas Removal Behaviors of Porous Carbons in the Presence of Ag/Ni Bimetallic Clusters

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Ag/Ni bimetallic cluster loading on porous carbon fibers was accomplished in order to enhance the HCl removal efficiency of the carbons. The surface properties of the Ag/Ni/carbons were determined by XRD and SEM. N_2/77 K adsorption isotherms were investigated using BET and Boer's t-plot methods. The HCl removal efficiency was confirmed by a gas chromatography technique, and it was found that that efficiency was predominantly improved in the presence of Ag/Ni clusters compared with the efficiencies of the as-received and single-metal-plated carbons. This indicates that synergetic reactions exist between Ag/Ni and HCl gas, resulting in advanced HCl removal capacity of porous carbons.

Key Words : Ag/Ni bimetallic cluster, Electroplating, Porous carbon fibers, HCl gas

Introduction

Air pollution has been aggravated by four developments: increasing traffic, urban growth, rapid economic development, and industrialization. Air pollution threatens the health of human beings and other life on our planet.[1-4] Especially, acidic gases, such as NO_x, SO_x, and HCl, as by-products of incineration processes, are major contributors to atmospheric pollution.[3-7] These gases can combine with some volatile organic compounds to produce smog or acid rain. One such gas, hydrogen chloride (HCl), is toxic, eroding metals, inducing cancer, and acting as a precursor of dioxin in the burning of trash. Not surprisingly therefore, there has been a strong push to remove those gases from domestic and industrial combustion processes.[4-9]

Porous carbons, such as activated carbons or fibers, can work as reducing agents, catalysts, and adsorbents in helping to eliminate air pollutants. When used as catalysts, porous carbons are normally impregnated with metal salts that can reduce the temperature required for the reduction of air pollutants. Recently, electrolytic metal plating (Cu^{10}, Ag^3, Ni^4, etc) on carbon surfaces has been proposed as a useful method for introducing metal nanoparticles (or clusters) onto carbon surfaces and into the porous structures of carbons.[2,12]

In our previous reports,[3,4,10] activated carbon fibers containing metal nanoparticles, such as Cu, Ag, and Ni, showed much higher adsorption capacities than those of as-received activated carbon fibers, due to the co-contribution of the high specific surface area of activated carbon fibers and the high reduction activity of the metal nanoparticles introduced. Metal plating on carbon surfaces is obviously different from metal impregnation, because metals loaded by plating are pure metals and not metal salts. When pure transition metal nanoparticles (or clusters) meet with HCl, the reaction occurs rapidly without any side reaction,

forming metal chlorides.[3] Several single metals plated by electro-metal plating have been studied with regard to their efficacy in hydrogen chloride removal. However, the effects of bimetallic cluster catalysts on HCl removal have not yet been exhaustively studied. In our previous work, we found that Ag and Ni nanoparticles on carbon fibers were so effective in HCl removal because they formed AgCl and $NiCl_2$, respectively, when they met HCl gas.

In this paper, we report the synergic effects of bimetallic catalysts composed of silver and nickel clusters on carbon surfaces in the removal of hydrogen chloride gas. Bimetallic catalysts were prepared according to different metal composition ratios.

Experimental

Preparation of porous carbon fibers. The porous carbon fibers used in this work were prepared by a CO_2 activation method[2,13] from untreated and unsized polyacrylonitrilebased fibers, TZ-307 (12 K), manufactured by Taekwang Co. of Korea. The activation temperature was 1100 °C and the CO_2 feeding rate was 100 cc/min. The textural properties of the 'as-received' porous carbon fibers are listed in Table 1.

Electroplating. For the electroplating of Ag and Ni metals, porous carbon fibers were fixed at a porous conductive plate in order to be used as an anode, and Ag or Ni plates were used as a cathode.[3,4,10] In the case of Ag plating, AgCN (30 g/L), NaCN (5 g/L), and $NaCO_3$ (10 g/L) solutions were used as electrolytes. The plating was accomplished at room temperature with 50 A/m². The amount of metal content was measured by atomic absorption spectrophotometry (AAS). The silver content was fixed at 5.2 wt.% in order to reduce variables, but the nickel content varied according to nickel plating times ranging from 1 to 5 min, and the electrolytes were composed of 30 g/L of $NiCl_2$ and

10 g/L of NiSO$_4$.

Microstructures. In order to study the surface structures of the bimetallic-clusters-loaded porous carbons, wide angle X-ray diffraction (XRD) patterns were obtained with a Rigaku Model D/MAX-III B diffraction meter equipped with a rotation anode using CuKα radiation ($\lambda = 0.15418$ nm). A Hitachi S-2400 scanning electron microscope (SEM) was used to observe the pore structures and surface morphologies of the porous carbons studied.

Textural properties. N$_2$ adsorption isotherms at 77 K were measured by ASAP 2010 (Micromeritics). Preparatory to that, the samples were outgassed at 573 K for 12 h to obtain a residual pressure of less than 1×10^{-6} mmHg. The amount of N$_2$ adsorbed on the porous carbons was used to calculate the specific surface area by means of the BET equation.[14,15] The total and micropore volume was estimated relative to the liquid volume of N$_2$ at a relative pressure of about 0.995 using Boer's *t*-plot method.[16-18]

Toxic gas removal. In order to measure the HCl removal efficiency of the samples, a gas chromatograph (DS 6200 model, Donam Co., Korea) with a thermal conductivity detector was used.[19] Before the HCl removal tests, all of the samples and a reactor were purged with high-purity N$_2$ gas (99.99%) at 298 K for 1 h in order to remove residual moisture. About 0.5 g of the samples was packed into a cylindrical quartz tube, and then HCl gas (concentration: 1013 ppm) was injected. The gas flow rate was maintained at 100 mL/min by a mass flow controller (GMC 1000, MKS). The HCl removal efficiency was determined from the concentration of HCl at the outlet reactor. Prior to each analysis, an HCl standard curve was obtained by using 300, 600, and 1000 ppm HCl gases.

Results and Discussion

Metal plating. The Ni contents, obtained from the AAS results for the Ag/Ni bimetallic-clusters-loaded porous carbons, are listed in Table 1 (the Ag content was fixed at 5.2 wt.%, as mentioned above). It was observed that the Ni content on the carbon surfaces was steadily increased to 30.5 wt.%. Table 1 shows the textural properties of each sample. It was easily determined that the specific surface area and pore volume were decreased, due to the blocking of pores by the loaded metal clusters.

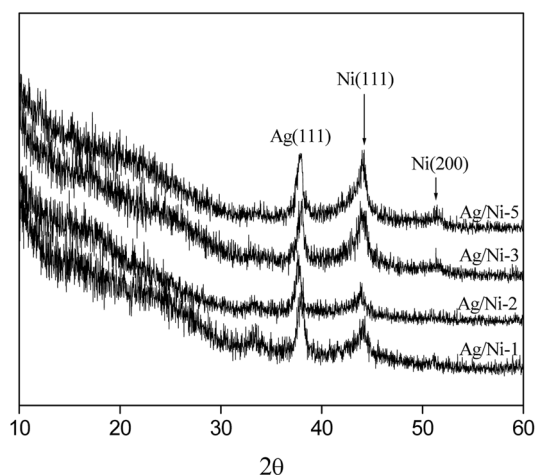**Microstructures.** Figure 1 shows the XRD patterns of the

Table 1. Metal Content and Textural Properties of Ag/Ni bimetallic cluster-loaded Porous Carbon Fibers

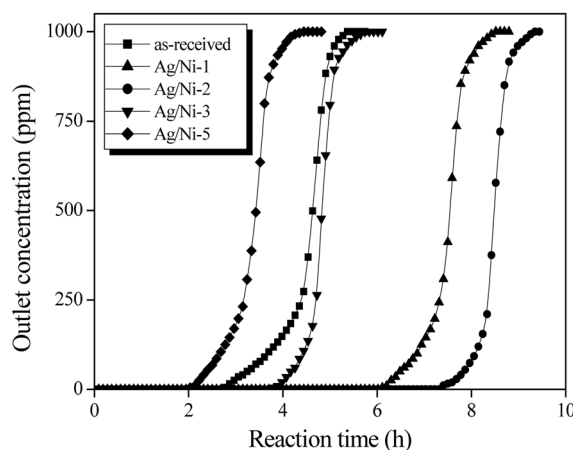| Sample	Ni content^a	S$_{BET}$^{b}	V$_T$^{c}	V$_M$^{d}
as-received	0	1980	1.20	0.80
Ag/Ni-1	7.5	1850	1.18	0.78
Ag/Ni-2	12.5	1740	1.15	0.75
Ag/Ni-3	22.5	1420	0.98	0.70
Ag/Ni-5	30.5	925	0.89	0.66

^{a}Ag content is fixed to 5.2 wt.% and Ni content is various as a function of Ni plating time. ^{b}Specific surface area (m^2/g). ^{c}Total pore volume (cm^3/g). ^{d}Micropore volume (cm^3/g)

Ag/Ni bimetallic-cluster-loaded porous carbon fibers. The Ag peaks were observed at $2\theta = 37^o$ (Ag 111), and the Ni peaks were observed at $2\theta = 44^o$ (111) and 51° (200). The intensity of the Ag peaks at 37° was almost regular. It was found that the Ni peaks at 44° were proportionally increased with the increase of the Ni plating times, indicating that the content of Ni in the Ag/Ni bimetallic clusters increased steadily.
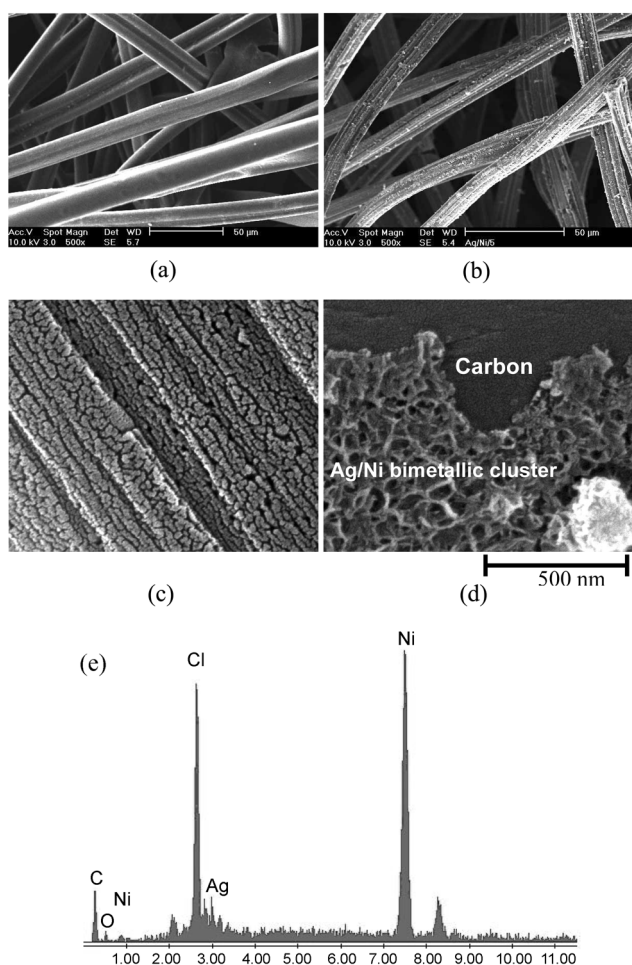
Toxic gas removal. Figure 2 shows the HCl removal efficiency of the Ag/Ni bimetallic-cluster-loaded ACFs. In the case of the as-received carbons, their capacity was exhausted after 30 min. Meanwhile, in the case of the Ag/Ni co-plated ACFs, the Ag/Ni-1 and Ag/Ni-2 samples showed an absolutely higher HCl removal efficiency than that of the as-received samples. However, the Ag/Ni-3 sample was similar to the as-received samples in HC1 removal efficiency, and the efficiency of the Ag/Ni-5 sample was even more diminished. This result can be explained by the fact that excessive metal plating of over Ni 22.5 wt.% can cause a decrease in HCl removal efficiency because of the severe pore filling behaviors, resulting in the decrease of specific surface area under 1400 m^2/g, meaning that the physical

Figure 1. XRD patterns of Ag/Ni bimetallic cluster-loaded porous carbon fibers.

Figure 2. HCl removal efficiency of Ag/Ni bimetallic cluster-loaded porous carbon fibers.

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respectively, and the metal contents were 22 wt.% and 5.2 wt.% for Ag and Ni, respectively. This indicates that Ag/Ni bimetallic-cluster-loading leads to the improved HCl removal efficiencies of 21% and 14% compared with single-metal loading.

Morphologies and surface composition. Figure 3 shows the SEM images of Ag/Ni bimetallic-cluster-loaded ACFs before and after metal plating as well as an EDX result after an HCl removal test. It was found that the grain-like Ag/Ni clusters were homogenously dispersed on the carbon surfaces, as seen in (b), and that the true image of the clusters was a net-like structure, as confirmed in (d). In the case of the EDX result, a chlorine peak was observed, indicating the successful formation of AgCl or $NiCl_2$ after an HCl test.

Conclusions

In the present study, bimetallic clusters were introduced onto porous carbon surfaces by Ag and Ni co-plating in order to enhance the HCl removal efficiency of porous carbons. It was concluded that the HCl removal efficiency of the porous carbons was predominantly advanced with the presence of Ag/Ni bimetallic clusters due to the synergetic co-reactions of Ag and Ni, compared with the as-received porous carbons or single-metal-loaded porous carbons.

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Figure 3. SEM images of the porous carbon fiber surfaces before and after Ag/Ni bimetallic cluster loading; (a) as-received, (b) Ag/Ni-5, (c) magnified picture of (a), (d) magnified picture of (c), and (e) an EDX result after HCl removal tests.

adsorption capacity of ACFs themselves, and also because Ni metals fully cover Ag metals, resulting in the prohibition of the co-reaction effects of Ag/Ni bimetallic catalysts.

Meanwhile, it was found that the sample presenting the best HCl removal efficiency was Ag/Ni-2 with 7.4 h of breakthrough time. This breakthrough time can be express by the breakthrough amount, such as 0.055, 0.017, 0.145, 0.042, and 0.039 g/g (HCl/metal-loaded ACFs) corresponding to as-received, Ag/Ni-1, Ag/Ni-2, Ag/Ni-3, and Ag/Ni-5, respectively.

This result proves that Ag/Ni bimetallic-cluster-loading with an appropriate metal content can improve the HCl removal efficiency of metal/ACFs in spite of the decrease in the specific surface area and pore volume of ACFs due to the synergistic co-reaction of Ag/Ni bimetallic clusters with HCl gas, which co-reaction can be represented by the following equation:

$$ACFs\text{-}Ag/Ni + 3HCl \rightarrow ACFs\text{-}AgCl/NiCl_2 + 3/2H_2 \quad (1)$$

In our previous work, the single-metal (Ag or Ni)-loaded ACFs showed quite good HCl removal efficiency. However, the best efficiencies of Ag[3] and Ni[4] were 6.1 h and 6.5 h,