

Influence of Nickel Electroplating on Hydrogen Chloride Removal of Activated Carbon Fibers

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Abstract

In this work, a nickel metal (Ni) electroplating on the activated carbon fiber (Ni/ACFs) surfaces was carried out to remove the toxic hydrogen chloride (HCl) gas. The surface properties of the treated ACFs were determined by using nitrogen adsorption isotherms at 77 K, SEM, and X-ray diffraction (XRD) measurements. HCl removal efficiency was confirmed by a gas-detecting tube technique. As a result, the nickel metal contents on the ACF surfaces were increased with increasing the plating time. And, it was found that the specific surface area or the micropore volume of the ACFs studied was slightly decreased as increasing the plating time. Whereas, it was revealed that the HCl removal efficiency containing nickel metal showed higher efficiency values than that of untreated ACFs. These results indicated that the presence of nickel metal on the ACF surfaces played an important role in improving the HCl removal over the Ni/ACFs, due to the catalytic reactions between nickel and chlorine.

Keywords : *activated carbon fibers, electroplating, hydrogen chloride, catalytic reaction*

1. Introduction

Air pollution is as follows – ‘The presence in the atmosphere of one or more contaminants in such quality and for such duration as is injurious, or tends to be injurious, to human health or welfare, animal or plant life’. It is the contamination of air by the discharge of harmful substances. Air pollution can cause health problems and it can also damage the environment and properties. It has caused thinning of the protective ozone layer of the atmosphere, which is leading to climate change. Modernisation and progress have led to air getting more and more polluted over the years. Industries, vehicles, increase in the population, and urbanization are some of the major factors responsible for air pollution [1, 2].

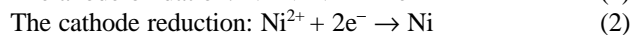
It has been well known that the hydrophilic gases, such as HCl, SO_x and NO_x, are major components of air pollution. Removal of HCl is essential since it is harmful, corrosive and an acid rain contributor. Moreover, HCl either directly or indirectly can lead to the formation of chlorinated hydrocarbons during chlorine containing plastics pyrolysis process, and it can use in military as weapons of mass destruction [3-5].

Porous carbon materials have been used in separation, purification, and catalytic processes due to their extended specific surface area, high adsorption capacity, microporous structure, and functional surface reactivity. The adsorption of

activated carbon fibers (ACFs) depends on many kinds of factors, such as raw materials, activation process, nature of pore structure, and surface functionalities [2, 6, 7].

Recently, there are several methods for prevention and control technique of air pollution. Many researchers have studied air pollution removal using activated carbons (ACs) or ACFs by metal electroplating, impregnation, sputtering, and so on [8-12].

Among these, an electroplating is the deposition of a metallic coating onto an object by putting a negative charge onto the object and immersing it into a solution which contains a salt of the metal to be deposited. In this work, the formation process of nickel-plating on the ACF surfaces can be represented by equation (1) and (2).



The aims of this work are to prepare nickel metal (Ni) plated ACFs (Ni/ACFs) from electroplating and to find the suitable reaction conditions. Also, HCl removal efficiency is analyzed by a gas-detecting tube technique.

2. Experimental

2.1. Materials and sample preparation

The activated carbon fibers (ACFs) obtained from Taiwan

Table 1. Composition and operating conditions of Ni electroplating bath

Composition	NiSO ₄ ·6H ₂ O	280 g·l ⁻¹
	NiCl ₂ ·6H ₂ O	40 g·l ⁻¹
	H ₃ BO ₃	30 g·l ⁻¹
Conditions	pH	4.5~5.0
	Temperature	25 ± 1 °C
	Current density	60 A·m ⁻²

Carbon Co. were used in this work. Before being plated, the ACFs were washed several times with distilled water and dried at 80 °C.

A nickel electroplating device was constructed that can continuously plate nickel onto the ACF surfaces. Electrolytic nickel plate was used as the anode and ACFs were used as the cathode to be plated. The ACFs were plated with different times 0, 1, 2, 3, and 5 minutes. The ACFs prepared from nickel electroplating were named as pristine, Ni-1, Ni-2, Ni-3, and Ni-5. The compositions and operating conditions of the plating bath were given in Table 1. The nickel content was measured by atomic absorption spectrophotometry (AAS).

2.2. Surface properties

A scanning electron microscope (SEM, JEOL JSM 840 A) was used to investigate surface morphologies of the ACF surfaces. In addition, wide-angle X-ray diffraction (XRD) patterns of the Ni/ACFs before and after nickel electroplating were obtained with a Rigaku Model D/MAX-III B diffraction meter equipped with a rotation anode using Cu-K_α radiation ($\lambda = 0.15418$ nm).

2.2.1. Textural properties

Nitrogen adsorption isotherms were measured using ASAP 2010 (Micromeritics) at 77 K. Prior to each analysis, the samples were out-gassed at 298 K for 9 h to obtain a residual pressure of less than 10⁻³ Pa. The specific surface area and the micropore volume were estimated by BET equation and *t*-plot methods, respectively [13, 14].

2.2.2. Hydrochloride removal

For the present experiment, two types of experimental technique were used for the detection of HCl removal behaviors. In case of low HCl concentration around 0~40 ppm at the outlet of reactor, a gas detecting tube (GASTEC: No. 14 L, range: 1~40 ppm) was used to measure HCl removal efficiency. All samples and the reactor were purged using N₂ gas (99.9999%) of high purity at 295~298 K for 1 h to remove residual moisture. About 0.1 g of the sample was packed with the cylindrical quartz tube and then HCl gas (concentration 1013 ppm) was injected. Gas flow rate was maintained at 10 ml/min by a mass flow controller

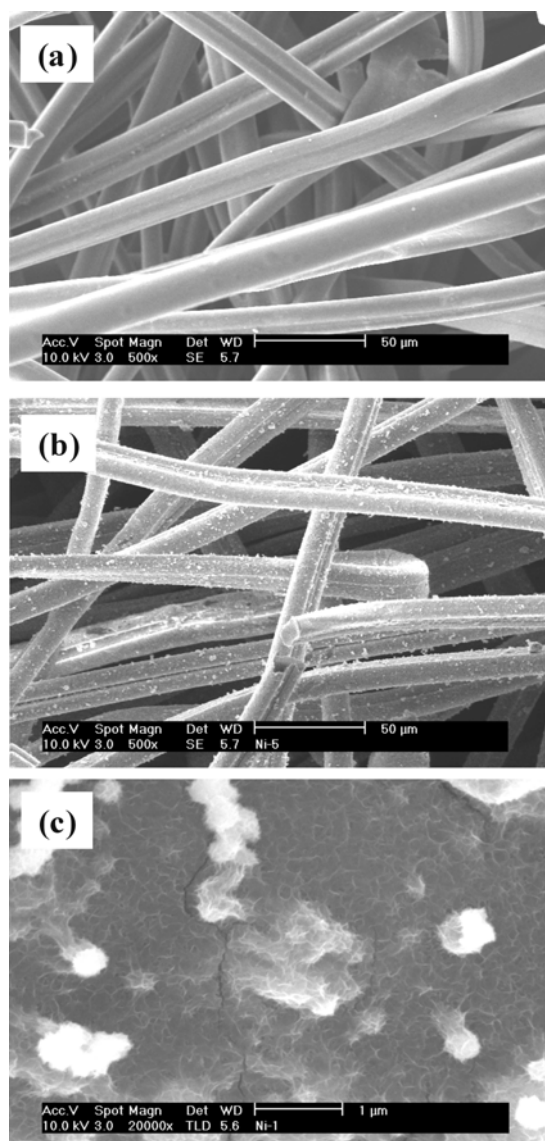
(GMC 1000, MKS). HCl removal efficiency was determined from the concentration of HCl at the outlet reactor.

3. Results and Discussion

3.1. Ni plating and surface properties

Table 2. Nickel quantification of the electrolytic Ni-plated activated carbon fibers

	pristine	Ni-1	Ni-2	Ni-3	Ni-5
Nickel Contents (wt.%)	0	1.6	2.3	5.5	6.3

**Fig. 1.** SEM images of the electrolytic Ni-plated activated carbon fibers. (a) pristine, (b) Ni-5, and (c) zoom image of Ni-1.

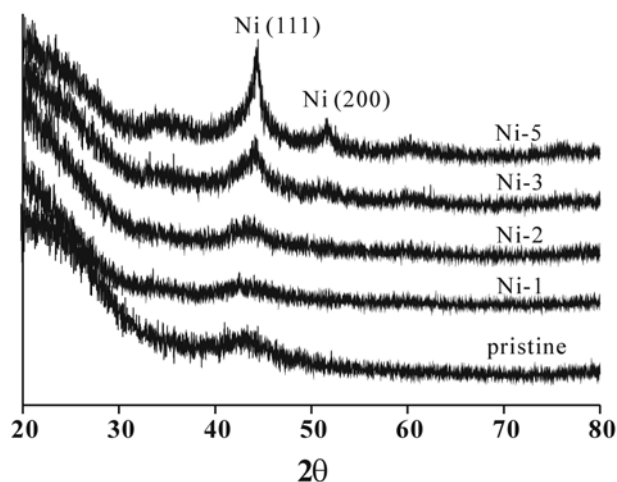


Fig. 2. X-ray diffraction profiles of the electrolytic Ag-plated activated carbon fibers.

Table 2 shows the content (wt.%) of nickel on the ACFs as a function of electroplating time. As seen in Table 2, the contents of nickel on the ACFs are linearly increased with increasing the plating time, but the plating rate is decreased gradually. It is demonstrated that the presence of nickel metal on the ACF surfaces [7].

Figure 1 shows SEM images of the Ni/ACFs ((a) pristine, (b) Ni-5, and (c) zoom image of Ni-1) before and after nickel electroplating. From the SEM images, Ni-5 was fully covered with nickel metal particles after electroplating. Figure 1(c) shows that the plated nickel metal particles on the ACF surfaces. It is revealed that the surface pore structures on ACFs undergo pore-blocking phenomena owing to deposition of nickel metal on the ACFs. And also that HCl gas can react more actively due to the nickel metal.

Figure 2 shows the wide-angle XRD patterns of the Ni/ACFs. As a result, the broad diffraction peaks around $2\theta = 20^\circ$ are investigated in carbon materials and nickel peaks are not observed in the pristine sample. However, the nickel peaks are observed in the Ni/ACFs. The sharp peaks around $2\theta = 44^\circ$ and 51° corresponding to (111) and (200) planes of nickel on the surface of the Ni/ACFs. Intensity of the carbon peak in the Ni/ACFs decreased, whereas nickel peaks and crystallinity in the Ni/ACFs are strengthened with extending plating time. Also, the nickel metal particle size is calculated by using the Scherrer equation [15]. As a result, the average size of nickel metal is 50~100 nm. As the electroplating proceeds, nickel metal nuclei migrate and aggregate to result in the formation nickel particle and then the particles grow to a greater size.

3.1.1. Textural properties

The results of nitrogen adsorption isotherms of the studied ACFs are shown in Figure 3. Their shape, as seen in Figure 3, indicates that the pore structures are approximately Type I

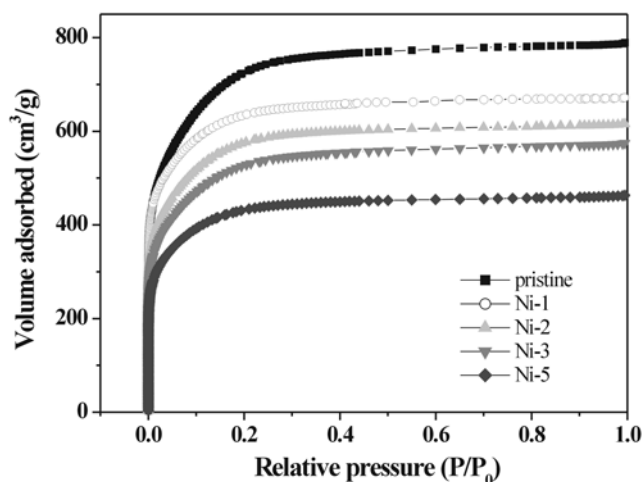


Fig. 3. Adsorption isotherms of N_2 at 77 K on the electrolytic Ni-plated activated carbon fibers.

Table 3. Textural properties of the electrolytically Ni-plated activated carbon fibers

Nomenclature	pristine	Ni-1	Ni-2	Ni-3	Ni-5
BET surface area [m^2/g]	2121	1974	1873	1788	1544
Micropore volume [cm^3/g]	1.15	0.86	0.85	0.79	0.69
Total pore volume [cm^3/g]	1.21	0.89	0.88	0.82	0.71
Fraction microporosity [%]	95	96	96	96	97

according to the IUPAC classification [16]. It is evident that most of the pore volumes of the samples are filled at low relative pressure about 0.1, indicating that these ACFs are highly microporous. Detailed information on the textural properties of the ACFs is listed in Table 3. It is clear that the nickel metal content has a considerable influence on the porosity development. As expected, the specific surface area, total pore volume, and micro pore volume decrease markedly with expanding plating time. It can be seen that nickel metal electroplating causes direct blockage of pores by the deposition of nickel metal on ACF surfaces.

3.1.2. Hydrogen chloride removal efficiency

Generally, chemical reactions can be classified according to the pattern of atomic rearrangements. The one of the most general reactions is combination reactions. In this case, two or more reactants combine to form a single product. For example, metals react with non metals to form the corresponding ionic compound. The reaction between sodium and chlorine is a good example. Also, the chlorine is a greenish yellow gas which combines directly with nearly all elements.

The activities of Ni/ACFs for HCl removal are shown in

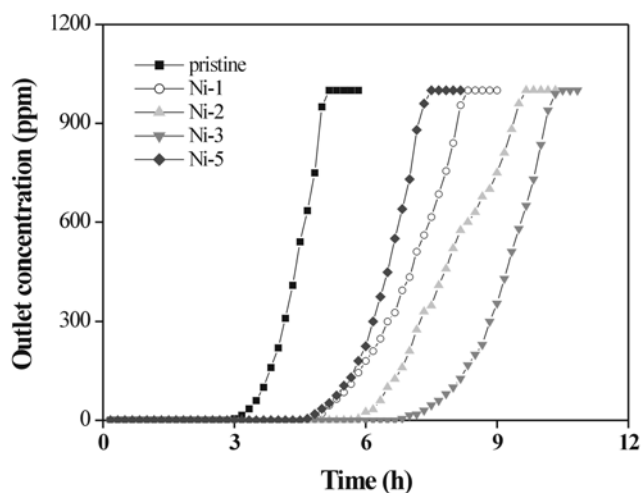


Fig. 4. HCl removal efficiency of the electrolytic Ni-plated activated carbon fibers.

Figure 4. The electrolytically Ni-plated ACFs show much higher removal efficiency than that of untreated ACFs, and Ni-3 sample shows the highest removal efficiency. This result means that the removal efficiency is depended on induced metal, but the specific surface area also affects it, as observed in Ni-5 sample.

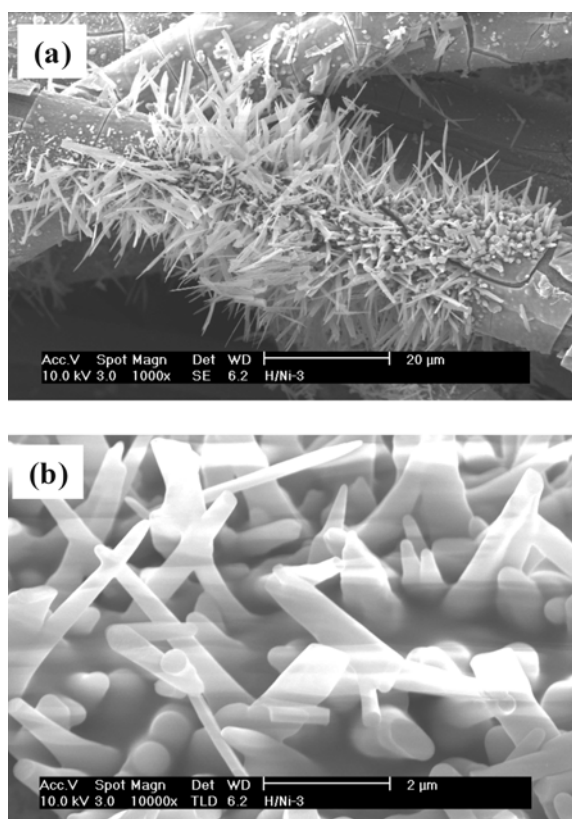


Fig. 5. SEM images of the H/Ni/ACFs after HCl removal tests. (a) H/Ni-3 and (b) zoom images.

Figure 5 shows the changes of the surface morphologies of the H/Ni/ACFs ((a) H/Ni-3 and (b) zoom image of H/Ni-3) after HCl removal tests. It is observed that many sharp particles appeared after the removal tests, compared to Figure 1(b) and (c). From the results, we suspect that the catalytic reaction is occurred by strong interaction between nickel and chlorine and formed ionic compound, such as NiCl_2 , during the HCl gas flow through the packed sample. The nickel, as an active site, takes part in HCl removal and enhances the removal efficiency.

4. Conclusions

The aims of this work were to prepare ACFs supporting nickel metal (Ni/ACFs) and to investigate the surface properties of the Ni/ACFs and HCl removal efficiency by using AAS, SEM, XRD, and gas-detecting tube techniques. From the AAS, SEM, and XRD results, it was found that the content of nickel on ACF surfaces was increased with increasing the plating time. Also, removal efficiency of HCl indicated that higher values on Ni/ACF samples, compared with untreated ACFs. These results indicated that the presence of nickel metal on ACF surfaces played an important role in improving the HCl removal, which could be explained by the presence of catalytic reactions between nickel and chlorine. Consequentially, nickel electroplating on ACFs was a useful technique for the improving removal efficiency of HCl.

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References

- [1] Noll, K. E.; Gounaris, V.; Hou, W. S. *Adsorption Technology for Air Water Pollution Control*; Lewis, Michigan, 1992.
- [2] Bansal, R. C.; Donnet, J. B.; Stoeckli, F. *Active Carbon*; Marcel Dekker, New York, 1998.
- [3] Arthur, C. S. *Air Pollution: Measuring, Monitoring, and Surveillance of Air Pollution*; ACADEMIC PRESS, New York, 1976.
- [4] Kasaka, S.; Sakata, Y.; Shirata, M. *Nippon Kagaku Kaishi*. **1977**, 11, 1728.

- [5] Kunio, K.; Hindenori, S. *J. Chem. Eng. Japan*. **1994**, *27*, 276.
- [6] Suffet, Y. H.; McGuire, M. J. *Activated Carbon Adsorption*; Ann Arbor Science, Michigan, 1981.
- [7] Park, S. J.; Shin, J. S. *J. Colloid Interface Sci.* **2003**, *264*, 39.
- [8] Chung, T. W.; Chung, C. C. *Chem. Eng. Sci.* **1999**, *54*, 1803.
- [9] Park, S. J.; Jang, Y. S. *J. Colloid Interface Sci.* **2001**, *237*, 91.
- [10] Wey, M. Y.; Fu, C. H.; Tseng, H. H.; Chen, K. H. *Fuel*. **2003**, *82*, 2285.
- [11] Chen, S.; Zeng, H. *Carbon*. **2003**, *41*, 1265.
- [12] Park, S. J.; Jin, S. Y. *Carbon*. **2004**, *42*, 2113.
- [13] Brunauer, S.; Emmett, P. H.; Teller, E. *J. Am. Chem. Soc.* **1938**, *60*, 309.
- [14] Lippens, B. C.; de Boer, J. H. *J. Catal.* **1965**, *4*, 319.
- [15] Cullity, B. *Elements of X-ray Diffraction*; Addison-Wesley, Amsterdam, 1988.
- [16] Sing, K. S. W.; Everett, D. H.; Hanl, R. A. W.; Moscou, L.; Pierotti, R. A.; Rouquerol, J.; Siemieniewska, T. *Pure Appl. Chem.* **1985**, *57*, 603.