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Electroless copper deposition on a pitch-based activated carbon fiber and an application for NO removal

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Abstract

Pitch fibers were prepared from petroleum-derived isotropic pitch precursors using melt-blown spinning. Activated carbon fibers (ACF) were formed from pitch fibers and after stabilization, carbonization and steam thermal activation were then further activated with Pd–Sn catalytic nuclei in a single-step process. The activated ACF were then used as supporters in the specific, electroless deposition of fine copper particles. Field emission scanning electron microscopy-energy dispersive X-ray spectroscopy results showed that the ACF were uniformly coated with nearly pure fine copper particles, and the copper content on the ACF increased with deposition time. The amounts of copper on the ACF and their crystalline characteristics were analyzed using an inductively coupled plasma and a X-ray diffractometry, respectively. With the copper particles-deposited on the ACF, the removal of nitrogen monoxide (NO) for four different deposition times (5, 10, 15 and 20 min) was tested. Experiments on the removal of NO were carried out in a packed bed tubular reactor with various reaction temperatures ranging between 423 and 673 K. For all deposition times, the NO removal efficiency increased with increasing reaction temperature up to 673 K. The NO removal efficiency was the highest when the amount was Cu/ACF = 110 mg/g (deposition time of 5 min), however, decreased at Cu/ACF beyond 110 mg/g (deposition times of 10, 15, 20 min) due to the decreased adsorption as a result of the increased amount of copper.

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1. Introduction

Porous carbon materials, due to their extensive specific surface area, high adsorption capacity, microstructure, and special surface reactivity, have been widely used in separation, purification, and catalytic processes [1]. Activated carbon fibers (ACF), highly microporous carbon materials [2–4], are commercially available in the form of fiber tows, cloths (fabrics), papers, mats and felts [5]. ACF have a larger micropore volume and a more uniform micropore size distribution than granular activated carbons (GAC) and; thus, are considered to have a larger adsorption capacity and greater adsorption and desorption rates [6–11].

The ACF may be packed or constructed to fit almost any geometry for almost any catalytic application and satisfies the requirements of high catalyst effectiveness and a low pressure drop for finely divided catalysts, but avoids the technical problems associated with powders. For example, the ACF may be employed for the removal of NO_x [12–16], but only physically adsorbs a limited amount of NO because of the weak interactions between the two [17,18]. The catalytic reduction of NO to N_2 and O_2 using ACF employing a transition metal (Ni, Fe, Cu, or Pd) prepared by the impregnation and precipitation of an aqueous solution of the metal, has previously been investigated [1], copper has been shown to possess the most efficient catalytic activity toward the reduction of NO to N_2 and O_2, both with and without O_2 [19,20].

Recently, electrolytic metal deposition, of an aqueous solution of metal ions, has been proposed as a useful method for the

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introduction of a metal onto carbon surfaces and into carbon micropores [1,21]. Electroless metal deposition is a kind of electrolytic metal deposition and can be effective for coating ACF [21–23]. Electroless metal deposition refers to the deposition of a metal onto a substrate, without an external electric current, via oxidation–reduction reactions [24]. The electroless deposition technique enables catalytic components to be easily and uniformly deposited in some channels of supporter with a complex configuration, provided that the deposition solution is in contact with the channel walls [25].

For the stable deposition of fine metal particles onto the ACF, the catalytic activation method proposed by Ang et al. [26] and Xu et al. [27] was employed. These two investigations studied the coating of carbon nanotubes with nickel and copper, respectively. The nanotubes were activated in one activation bath (single-step process). In our study, a single-step process was used to catalytically Pd–Sn activate the ACF and; thus, to introduce metallic Pd sites onto the ACF surfaces for the electroless copper deposition [28]. The metallic Pd sites worked effectively in the electroless deposition of copper due to the galvanic displacement of the metallic Pd by Cu [24,29].

In the present study, pitch-based ACF were first coated with fine particles using electroless copper deposition and then characterized by field emission scanning electron microscopy (FESEM), energy dispersive X-ray spectroscopy (EDX), X-ray diffractometry (XRD), nitrogen adsorption and inductively coupled plasma (ICP) analysis. Finally, the effect of the copper particles on the catalytic reduction of NO was investigated at various reaction temperatures in the absence of oxygen.

2. Experimental

Pitch-based ACF were synthesized using a conventional melt-blown spinning method. The fibers, 1 mm in diameter, were produced, using extruding melt (IPP; SK Chemical Co., Korea) through a round-shaped mono-hole spinneret ($L/D=2$, $D=70$ mm), under pressurized nitrogen at 6 kg/cm^2, 673 K, with subsequent drawing at a take-up speed of 550 m/min. The melt-blown spinning pitch fibers were then oxidatively stabilized in air by heating to 673 K at 1 K/min for 2 h. The stabilized pitch fibers were then carbonized by heating in an N_2 atmosphere to 1273 K at 10 K/min for 30 min. After holding the carbonized fibers at 1223 K for 30 min, they were finally activated in steam (50 vol.%) carried by N_2. These ACF were washed with deionized water and dried overnight at an ambient temperature.

Since the bond strength of the copper particles on the ACF was very sensitive to surface contamination, the ACF were thoroughly degreased by immersing in a diluted degreasing agent bath (50 mL of CC829, Yooil Material Technology, Korea, mixed with 950 mL of DI water) at 327 K for 10 min. After washing the degreased ACF three times with DI water, the palladium and tin species were introduced onto by immersing in a mixed Pd–Sn colloidal solution at 318 K for 6 min. A solution (30 mL of CATA1064, Yooil Material Technology, Korea) diluted with 1 M of nitric acid (970 mL) was used as a mixed Pd–Sn colloidal solution. The catalytically activated ACF were immersed in an acceleration solution bath (50 mL ACCEL95, Yooil Material Technology, Korea, diluted to 1000 mL with DI water) for 7 min at 298 K and then washed with DI water a further three times. The acidic accelerator was used to preferentially dissolve the protective layer (mainly Sn layer), exposing a greater surface area of the catalytic Pd nuclei. When the catalytically activated, accelerated ACF were immersed in an electroless deposition bath, copper was deposited at the catalytic sites, with copper particles-deposited ACF finally obtained. The deposition bath (1 L) consisted of copper sulfate dominant solution (120 mL EC1051A, Yooil Material Technology, Korea, diluted to 500 mL with DI water) and formaldehyde dominant solution (110 mL EC1051B, Yooil Material Technology, Korea, diluted to 500 mL with DI water) at 298 K for various treatment times ranging from 0 to 20 min.

To study the surface structures of the ACF, wide-angle XRD patterns of the ACF were obtained with a Rigaku Model D/MAX-Rint 2000 (Japan) diffraction meter using Cu$K\alpha$ radiation ($\lambda=0.15418$ nm) at 30 kV and 20 mA. A thin powder sample of the ACF was placed onto an oriented monocrystalline quartz plate and scanned from 10° to 80° (2θ) at 4°/min. A FESEM (JSM-6500F, JEOL, Japan) was used to observe the surface morphology of the ACF as well as the distribution of copper particles. A chemical analysis was performed using EDX (JED-2300, JEOL, Japan). The amount of copper particles on the ACF sample was determined using an ICP (Elan 6000, Perkin–Elmer, US). Approximately 0.1 g of the sample was dissolved in

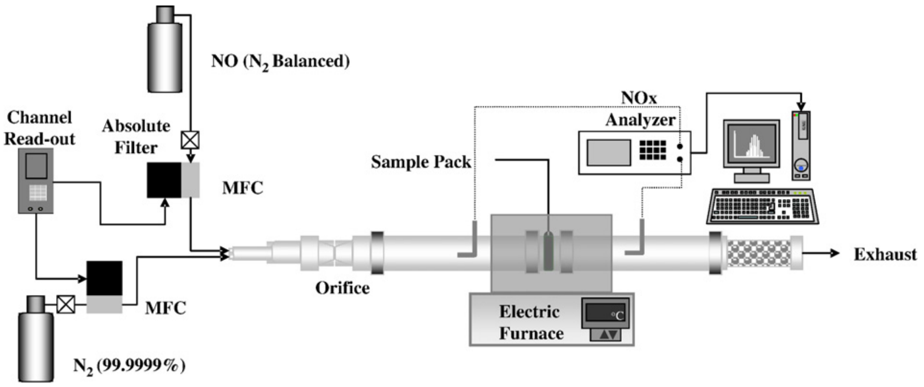

Fig. 1. Diagram of experimental set-up for NO removal test.