Thermal Decomposition of Hydrated Copper Nitrate [Cu(NO$_3$)$_2$·3H$_2$O] on Activated Carbon Fibers

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Abstract

Thermolysis of Cu(NO$_3$)$_2$·3H$_2$O impregnated activated carbon fiber (ACF) was studied by means of XRD analysis to obtain Cu-impregnated ACF. Cu(NO$_3$)$_2$·3H$_2$O was converted into Cu$_2$O around 230 °C. The Cu$_2$O was reduced to Cu at 400 °C, resulting in ACF-C(Cu). Some Cu particles have a tendency to aggregate through the heat treatment, resulting in the ununiform distribution in ACF. Catalytic decomposition of NO gas has been performed by Cu-impregnated ACF in a column reactor at 400 °C. Initial NO concentration was 1300 ppm diluted in helium gas. NO gas was effectively decomposed by 5~10 wt% Cu-impregnated ACF at 400 °C. The concentration of NO was maintained less than 200 ppm for 6 hours in this system. The ACF-C(Cu) deoxidized NO to N$_2$ and was reduced to ACF-C(Cu$_2$O) in the initial stage. The ACF-C(Cu$_2$O) also deoxidized NO to N$_2$ and reduced to ACF-C(CuO). This ACF-C(CuO) was converted again into ACF-C(Cu) by heating. There was no consumption of ACF in mass during thermolysis and catalytic decomposition of NO to N$_2$ by copper. The catalytic decomposition was accelerated with increase of the reaction temperature.

Keywords : activated carbon fiber, hydrated copper nitrate, metal impregnation, thermolysis

1 Introduction

Nitric oxide (NO) produced as a result from side reaction of high temperature combustion is an important atmospheric pollutant [1, 2]. It is necessary to investigate effective methods for removing NO from the atmospheric environment. There are many studies on the removal of nitrogen oxides through unharmful species such as N$_2$ and O$_2$. Among them, the selective catalytic reduction (SCR) of NO in flow gases from various sources is known as the most applicable technology, by using reducing agents such as CO, H$_2$, NH$_3$, and aliphatic carboxylic acid [3, 4]. But the disadvantage of this process is that it requires a complex and expensive setup for safely handling NH$_3$, which is a hazardous chemical [5] and results in catalyst plugging, fouling, or poisoning in the processing of it [6].

In recent years, to overcome these problems, theoretical and applied aspects of the catalytic decomposition of NO by the metal (Ni, Fe, Co, Cu, K, Ca and Na) on carbon prepared by impregnation with an aqueous solution of nitrate or acetate of metal have been elucidated in researches [7-9]. Especially, copper metal shows the most efficient catalytic activity toward the reduction of NO onto N$_2$ and O$_2$ either in the presence of O$_2$ or in the absence of O$_2$ [9].

Activated carbons are promising materials that can contribute to NO removal not only as a catalyst support, a decomposition reactant of NO to N$_2$, but also as an adsorbent for concentration of diluted NO [2, 9, 10]. ACF has more uniform slit-shaped micropores in comparison with granular AC [11]. Park [12] reported that Cu supported ACF shows good removal efficiency. Yoshikawa [13] and Kaneko [14, 15] reported that MnO$_2$ and iron oxide dispersed ACF can reduce large amounts of NOx at low temperature. However, ACF is a newly developed adsorbent and not so much reports compared with activated carbons in using catalyst supports for the removal of atmospheric pollutants.

Cu(NO$_3$)$_2$·3H$_2$O is one of the most popular precursor components, used in the preparation of various materials including high temperature superconductors and copper catalyst. However, the character of its thermal decomposition depends greatly on the processing conditions: on the pressure and temperature. Many investigators [16-18] observed two or three stages of thermolysis at atmospheric pressure: melting of hydrate at 116~152 °C; formation of β-Cu$_2$(OH)$_3$-NO$_3$ (199~217 °C) and its decomposition to CuO (263~310 °C [18]). Thermal decomposition of Cu(NO$_3$)$_2$·3H$_2$O at reduced pressures was performed in the solid state [19-21]. The final product of decomposition is CuO (T=182~312 °C [19], 247~260 °C [20]).

In this paper, decomposition of Cu(NO$_3$)$_2$·3H$_2$O impregnated on ACF was investigated as the increase of temperature at atmospheric pressure to obtain CuO, Cu$_2$O and Cu

impregnated activated carbon fibers.

2 Experimental

Cellulose-based ACF (KF-1500, Toyobo Co. Japan, 1497 m^2/g) was wet-chopped to 3~4 mm length, added to different concentration of $Cu(NO_3)_2 \cdot 3H_2O$ solution for 2 hour, room temperature, 200 rpm. Then, the ACF was laid on wire mesh until no dropping of solution, weighed and dried for over-night at 50 °C in a vacuum dryer. The impregnated amount of $Cu(NO_3)_2 \cdot 3H_2O$ on ACF was calculated from the increase of weight and the final content of Cu particle was calculated from the increment and concentration of $Cu(NO_3)_2 \cdot 3H_2O$. Investigation of thermal decomposition of the $Cu(NO_3)_2 \cdot 3H_2O$ by classical differential thermal analysis (TG/DTA) has been performed by increasing the temperature up to 600 °C at heating rate 10 °C min^{-1} in atmospheric pressure. One set of ampoules was heated up simultaneously. When the temperature 105, 160, 200, 230, 255, 300, 350, and 400 °C were achieved, corresponding ampoules were quenched and sealed off for further XRD study. XRD analysis has been performed using DRON-4 diffractometer at Cu-K_α radiation. The adsorption characteristics of Cu-impregnated ACFs were measured by N_2 adsorption at 77 K. SEM and TEM observations were carried out to investigate the morphology and scattering of Cu particles on ACF surface.

3. Results and Discussion

3.1. Decomposition of hydrated copper nitrate [Cu(NO₃)₂· 3H₂O] on ACF

Fig. 1 shows the TGA curves of 10 wt% $Cu(NO_3)_2 \cdot 3H_2O$ impregnated ACFs in air and N_2 atmosphere. The stage I of weight loss starts around 50 °C and finished at 160 °C due to the dehydration, resulting in the formation of $Cu_2(OH)_3NO_3$ like other researchers reports [16-21], although the formation temperature ranges were different from the processing conditions. Many researchers reported that anhydrous $Cu(NO_3)_2$ was formed with evolution of $H_2O_{(g)}$ and $HNO_{3(g)}$ in early stage. However, the anhydrous $Cu(NO_3)_2$ was sublimated to gas phase and not observed among solid intermediates [19, 21]. Also, the released $HNO_{3(g)}$ is transformed into NO_2, H_2O and O_2. To explain this phenomenon, along with sublimation, the mechanism of trapping of gaseous thermohydrolysis products by solid state particles because of "crystal rearrangement" have been proposed [22]. Morozov *et al.* [21] reported that there were four solid intermediates: α-$Cu(NO_3)_2$ and β-$Cu(NO_3)_2$, α-$Cu_2(OH)_3NO_3$ and amorphous copper hydroxonitrate. There was large amount of gas evolution in the stage I. A slow weight loss was progressed between 150~200 °C. The stage II of slow in N_2 and sudden weight loss in air surrounding was detected between 200 to 255 °C accompani-
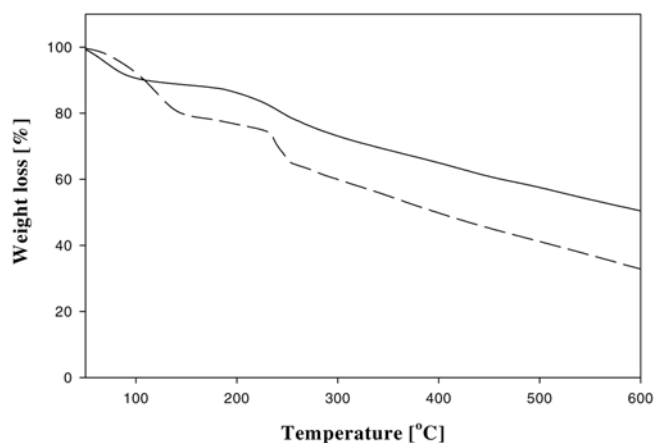

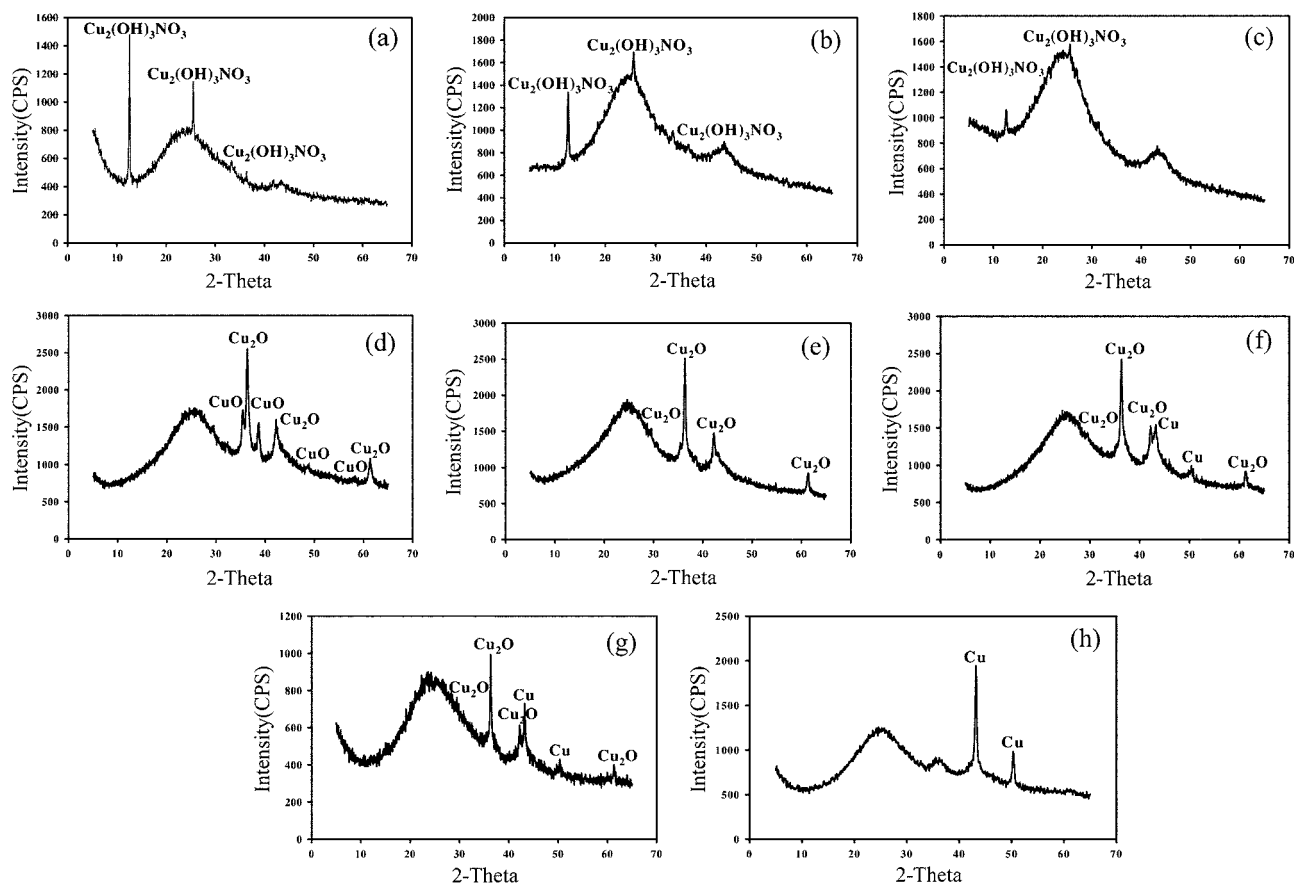**Fig. 1.** TGA curves of $Cu(NO_3)_2 \cdot 3H_2O$ impregnated ACFs in N_2 (——) and air (---).

ed by the decomposition of $Cu_2(OH)_3NO_3$.

Fig. 2 shows the XRD profiles of $Cu(NO_3)_2 \cdot 3H_2O$ impregnated ACFs, heated for 30 min. at (a) 105, (b) 160, (c) 200, (d) 230, (e) 255, (f) 300, (g) 350, and (g) 400 °C. The $Cu_2(OH)_3NO_3$ was only detected up to 200 °C, but CuO was formed over 200 °C by decomposition of $Cu_2(OH)_3NO_3$ and the mixture of CuO and Cu_2O was detected at 230 °C. At the 255 °C, only Cu_2O was detected. Many researchers did not reported the formation of Cu_2O between 200 to 300 °C. However, Marquez-Alvarez [8] has reported the detection of Cu_2O in this temperature range. This Cu_2O was gradually transformed into Cu after 300 °C and completely transformed into Cu at 400 °C, resulting in the formation of ACF-$C_{(S)}$(Cu) on the ACF surface. There was no detectable weight loss on activated carbon fibers during the decomposition of $Cu(NO_3)_2 \cdot 3H_2O$ into Cu particles.

Table 1 shows the products of $Cu(NO_3)_2 \cdot 3H_2O$ decomposition with respect to temperature prepared by some researchers. Despite common features observed in some studies, their interpretation is markedly different.

3.2. Characteristics of Cu-impregnated ACFs

Table 2 shows the characteristics of Cu-impregnated ACFs, which were obtained from heat treated for 30 min. at 400 °C. The BET specific surface area, total pore volume and the micropore volume decreased as the amount of Cu-impregnation increased, resulting in the increase of average pore diameter. Nishi [15] reported similar results in the impregnation of Cu-particles on ACFs. It was known that Cu particles blocked the entrance of some narrow micropores. Micropores of ACF was uniformly developed on the fiber surface. Therefore, Cu particles seemed to be uniformly distributed. Nevertheless, the ACFs have great potential as adsorption materials being the type I isotherm, within the range of well-developed micropores according to the BET classification.

Fig. 2. XRD profiles of $Cu(NO_3)_2 \cdot 3H_2O$ impregnated ACFs, heated for 30 min. at (a) 105, (b) 160, (c) 200, (d) 230, (e) 255, (f) 300, (g) 350, and (h) 400 $^{\circ}$C in N_2 atmosphere.

Table 1. Products of thermal decomposition of $Cu(NO_3)_2 \cdot 3H_2O$ with respect to temperature

| Temp. ($^{\circ}$C)	40-80	80-110	116-152	120-150	167-205	199-217	200-250	247-260	263-310
D.D.Perlmutter [18] (reduced Pressure)			Melting to $Cu(NO_3)_2$			$Cu_2(OH)_3NO_3$			CuO
D.Dollimore [19]	$3Cu(NO_3)_2 Cu(OH)_2$				182~312 CuO				
B.V.Lvov [20]					$Cu_2(OH)_3NO_3$			CuO	
I.V.Morozov [21] (reduced P=1Pa)	$Cu(NO_3)_2 \cdot 2.5 H_2O$ $Cu(NO_3)_2 H_2O$	Melting to $Cu(NO_3)_2$		Sublimation			CuO		
This study		80-150 Melting 105 $Cu_2(OH)_3NO_3$			160-180 $Cu_2(OH)_3NO_3$	200 CuO 230-255 CuO/Cu_2O		255 Cu_2O 300-350 Cu_2O/Cu	

Fig. 3 shows the SEM photos of Cu-impregnated ACF surface. The amounts of surface-adsorbed Cu particles increased as the increase of copper oxide compound concentration. Some Cu particles have a tendency to aggregate through the heat treatment resulting in the ununiform distribution of Cu particles. Fig. 4 shows the TEM photo of 5 wt% Cu-impregnated ACF. Some Cu particles have intruded into ACF micropores during the heat treatment.

### 3.3. Decomposition of NO through Cu-impregnated ACF packing column
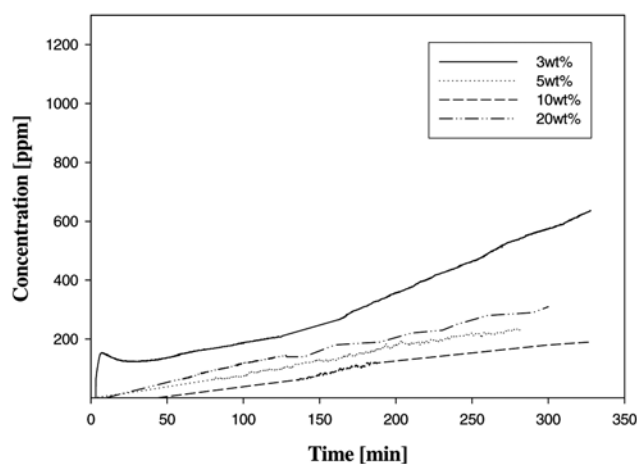
Fig. 5 shows the breakthrough curves of NO on as received ACFs at 20 $^{\circ}$C and 300 $^{\circ}$C. The breakthrough times were very short and both curves were steep just after the breakpoints, which means that the adsorption capacity of NO on ACF was very poor in spite of large specific surface area. The breakthrough time of NO at 300 $^{\circ}$C was shorter than

Table 2. Characteristics of Cu-impregnated ACF

ACF (wt%)	BET surface area (m²/g)	Total pore volume (cc/g)	Micropore volume (cc/g)	Average pore dia. (Å)
Cu- 0	1497	0.83	0.79	14.9
Cu- 3	1270	0.51	0.50	16.1
Cu- 5	1146	0.46	0.45	16.1
Cu-10	1005	0.42	0.40	16.5
Cu-15	797	0.34	0.32	16.8
Cu-20	659	0.31	0.28	18.5

(a)　(b)

(c)　(d)
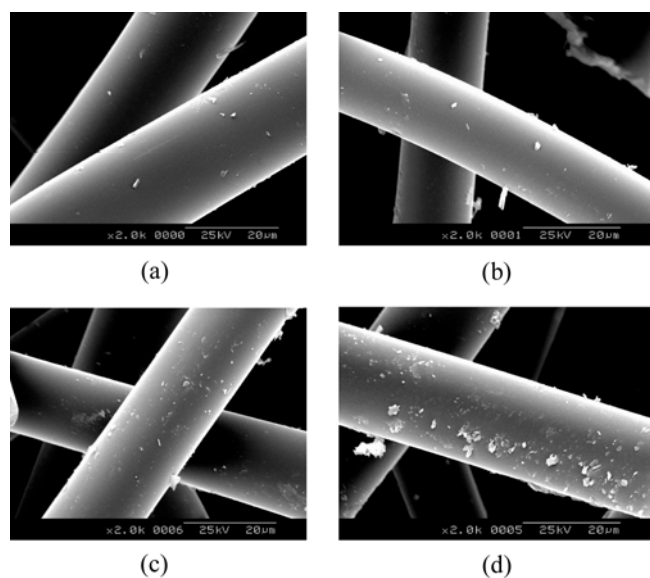
Fig. 3. SEM photos of Cu-impregnated ACFs, (a) 3 wt%, (b) 5 wt%, (c) 10 wt%, (d) 20 wt%.
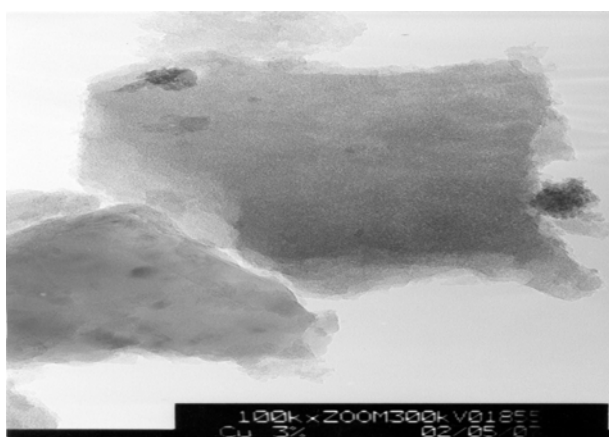

Fig. 4. TEM photos of 5 wt% Cu-impregnated ACFs.

that of NO at 20 °C. This is because the micropore field of carbon is not strong as to adsorb supercritical gases. A little amount of CO gas was detected at 300 °C indicated that NO gas was reacted with some functional groups at this temper-
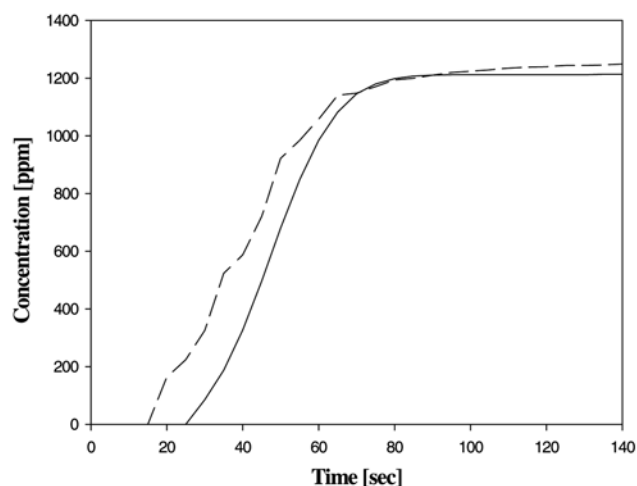
Fig. 5. Breakthrough curves of NO on ACFs at (a) 20 °C (——) and (b) 300 °C (---), ρ = 0.06 g/cm³, C_i = 1300 ppm, 3.0 l/min.

Fig. 6. Breakthrough curves of NO on Cu-impregnated ACF at 400 °C, ρ = 0.06 g/cm³, C_i = 1300 ppm, 3.0 l/min.
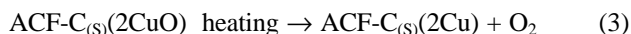
ature.

Fig. 6 shows the breakthrough curves of NO on Cu-impregnated ACFs at 400 °C. NO gas was effectively decomposed for a very long time. Also, the 10 wt% Cu-impregnated ACF shows the lowest NO concentration in the outlet stream, however the 5 wt% Cu-impregnated ACF decomposed NO gas very well too, even though the impregnated amounts was far smaller than 20 wt% ACF. Yoshikawa [13] reported that NO conversion by catalytic reaction with transition metal-oxides was directly proportional to the amount of impregnated catalysts and the reaction temperature.

Fig. 7 shows the XRD profiles of the 10 wt% Cu-impregnated ACFs at 400 °C before catalytic reaction, after reaction with NO and regeneration of Cu by heating from CuO. The profile (a) shows only the Cu peaks at 2θ = 43.3 and 50.5 before catalytic reaction. The profile (b) shows Cu₂O peaks at 2θ = 36.4, 42.3, and 61.3 besides Cu peaks after reaction with NO for 325 min., which means some of
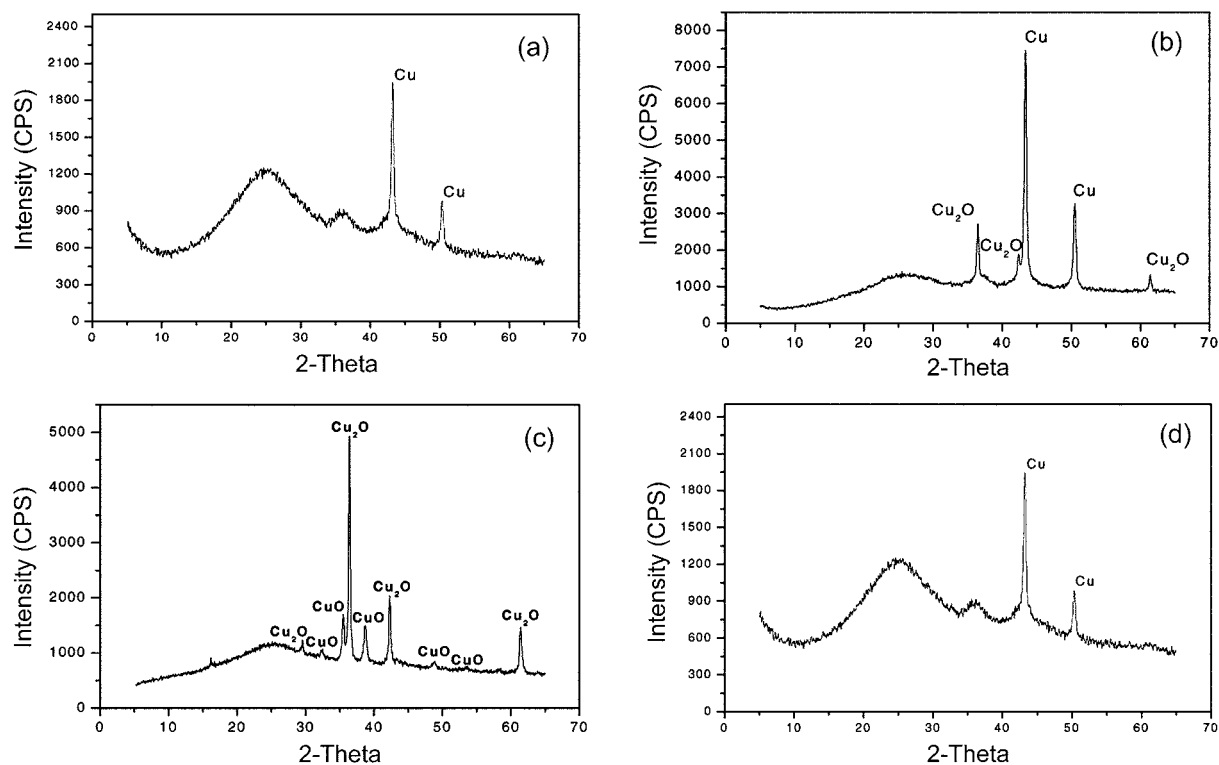
Fig. 7. XRD profiles of the Cu-impregnated ACFs at 400 °C, (a) before reaction, (b) after reaction with NO, 325 min., (c) 900 min., and (d) regeneration of (c) by heating in N_2.

Cu particles converted into Cu_2O during the first catalytic reaction stage with NO gas at 400 °C. The profile (c) shows that Cu_2O converted into CuO during the second catalytic reaction stage with NO gas. The profile (d) shows the regeneration of Cu-impregnated ACFs from CuO-containing ACFs. Park and Jang [23] reported that there was no CuO peaks during the NO decomposition by ACF/Cu catalyst at 400. However, Marquez-Alvarez et al. [13] have reported the existence of Cu_2O by the carbon-supported copper catalytic removal of NO. There was no consumption of ACF in mass during the catalytic decomposition of NO to N_2 by copper because of helium atmosphere. Therefore, following NO decomposition mechanism can be suggested by Cu-impregnated ACF.

$$ACF\text{-}C_{(S)}(2Cu) + NO \rightarrow ACF\text{-}C_{(S)}(Cu_2O) + 1/2\ N_2 \quad (1)$$

$$ACF\text{-}C_{(S)}(Cu_2O) + NO \rightarrow ACF\text{-}C_{(S)}(2CuO) + 1/2\ N_2 \quad (2)$$

$$ACF\text{-}C_{(S)}(2CuO)\ \text{heating} \rightarrow ACF\text{-}C_{(S)}(2Cu) + O_2 \quad (3)$$

4. Conclusions

Cu-impregnated activated carbon fiber is useful for the catalytic decomposition of some air pollutants in a high temperature combustion. $Cu(NO_3)_2 \cdot 3H_2O$ is one of the most popular precursor components in the preparation of copper catalyst. However, Cu-impregnation on activated carbon fiber from $Cu(NO_3)_2 \cdot 3H_2O$ solution should be carefully carried out, especially careful in drying and heating process, due to the formation of various copper compounds during the thermolysis. The Cu-impregnated ACF can be obtained by heating $Cu(NO_3)_2 \cdot 3H_2O$ up to 400 °C, which was effectively decomposed NO gas to N_2, reducing themselves to Cu_2O and CuO.

These Cu_2O and CuO can be converted again into Cu by simple heating. The catalytic decomposition was accelerated with increase of the reaction temperature.

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