

THE MANGANESE OXIDE PHASE STUDY ON THE DECOMPOSITION MECHANISM OF FORMALDEHYDE AND LONGEVITY

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Introduction

The present authors have studied new removal method of formaldehyde (HCHO) of indoor pollution gas at room temperature which is made by combining manganese oxide as a catalyst and PAN based activated carbon nanofiber (ACNF) as a support. The shallow micropores uniformly distributed on the ACNF support are expected to facilitate mass transport of formaldehyde while manganese catalyst on the surface would oxidize efficiently the effluent HCHO molecules.

Experimental

Electrospun PAN-based nanofiber with diameter of 800nm was received from Nanotechnics Co. Ltd., Korea and commercialized PAN-based activated carbon fiber samples were purchased (FE100 and FE300, TOHO TENAX, Japan) for comparison. Stabilization was implemented on the raw PAN nanofiber cloth at 270 °C for 9hs with the heating rate of 0.5 °C/min. The stabilized sample was activated through steam activation at 600 °C with the heating rate was 10 °C /min. The precursor for MnOx compound was selected to be manganese (II) acetate tetrahydrate (Mn(CH₃COO)₂·4H₂O, Wako Pure Chemical Industries, Japan). Based on its molecular ratio, Mn(CH₃COO)₂·4H₂O and PAN-based activated carbon nanofiber were mixed in ethanol and the solution was magnetic-stirred for 40hs at room temperature. The mixed sample was then placed in air oven at 80 °C to remove the solvent. The dried sample was then heat-treated at 380 °C for 10 min in air flow of 50ml/min to transform the manganese precursor into MnOx. The phase and statues of MnOx compound was confirmed through X-ray diffraction method.

Nitrogen isotherms of the samples were measured at 77K using BELSORP-max-S(BEL Japan Inc.). Surface areas were calculated by α -S method theory and their pore size distributions were obtained using non-local density functional theory(NLDFT) method. SEM images were taken using JSM-6700F(JEOL Japan Inc.) X-ray diffraction was carried out to characterize the phase of impregnated manganese oxide compounds using UltimaIII (Rigaku Japan Inc.).

A fixed-bed reactor unit was setup to identify adsorption measurement of formaldehyde. 50 mg of each sample was prepared and loaded into a narrow cylindrical glass tube (OD: 6mm, ID: 4mm and Height: 80mm). The container was

selected to maintain the feedstock's ratio of its diameter and height to be between 1:4 and 1:6. The proportional ratio was confirmed to ensure a correct evaluation condition without causing pressure drop. After the sample tube was set in air bath at constant 30 °C, the mixture of gases were introduced to penetrate the sample. The total flow rate was 100 ml/min. 20 ppmv of formaldehyde gas balanced with N₂ was obtained from Asahi sanso company, Japan. and was later diluted with air to have its outlet concentration 10 ppmv. After the reaction on the sample, the resultant outlet gas was later measured by formaldehyde detection sensor (Interscan Co. Model:4160) to check the breakthrough time. The breakthrough time was defined as the time at which the outlet concentration of formaldehyde reaches up to 5% of the total which is 0.5ppmv.

Results

Table1 lists the pore characteristics of PAN-based activated carbon fiber and activated nanofiber samples based on nitrogen adsorption isotherms. It was made clear that the amount of manganese oxide particles had diminished the overall surface area of samples. 5% of MnOx had decreased the surface area by approximately 50%.

TABLE I
Porous Structure Parameters and Formaldehyde breakthrough time of samples

Sample/ MnOx(%)	S _{acr} (m ² /g)	V _{total} (cm ³ /g)	Pore size (nm)	Breakthrough time(h)-R.H.0%	Breakthrough time(h)-R.H.90%
PANACNF					
0%	487	0.18	0.74	6.46	5.00
0.5%	477	0.15	0.63	9.98	4.66
1%	451	0.13	0.58	11.21	4.83
5%	255	0.10	0.78	12.47	10.33
20%	162	0.04	0.49	11.13	7.00
FE100					
0%	557	0.17	0.61	3.1	<1
0.5%	513	0.14	0.55	4.96	<1
1%	484	0.13	0.54	4.83	<1
5%	495	0.19	0.77	4.38	<1
20%	354	0.12	0.68	4.58	<1
FE300					
0%	777	0.45	1.16	2.17	<1
0.5%	755	0.42	1.11	1.88	<1
1%	740	0.40	1.08	2.59	<1
5%	641	0.42	1.31	5.91	<1
20%	218	0.06	0.55	1.19	<1

S_{acr}: Calculated from T-plot method between 0 and 0.5 t/nm; V_{total}: total pore volume calculated by equilibrium from T-plot; formaldehyde breakthrough time was calculated from breakthrough curves when the concentration reached 1ppm. R.H: Relative humidity from 0-90%

High resolution images of the PAN-based activated carbon nanofiber samples were observed under scanning electron microscope (SEM) (Figure 1) As can be observed from the 5% and 20% images, it was confirmed that the manganese oxides were roughly dispersed on the surface of activated carbon nanofibers (ACNFs). Compared to ACNF, the impregnated samples were seen as covered with manganese oxide in a shape of cloud forms. Fig. 2 illustrates the X-ray diffraction spectra of manganese oxides according to their impregnation contents on PAN ACNFs. The strong diffraction peaks at 2 θ values of 28.880, 32.316, and 36.086° representing the crystal planes of (112), (103), and (211) which majorly confirmed the formation of Mn₃O₄ particles. Other regions of peaks with comparatively low intensity were assigned to MnO and MnO₂ compounds. Some

MnO peaks were also found at 2θ values of 34.910 , 40.548 and 58.723° showing the crystal planes of (111), (200), and (220). The obtained XRD spectra provides a good indication that the heat treatment of the precursor, manganese (II) acetate tetrahydrate had been transformed into mostly MnO and Mn_3O_4 compounds by slight oxidation process in air.

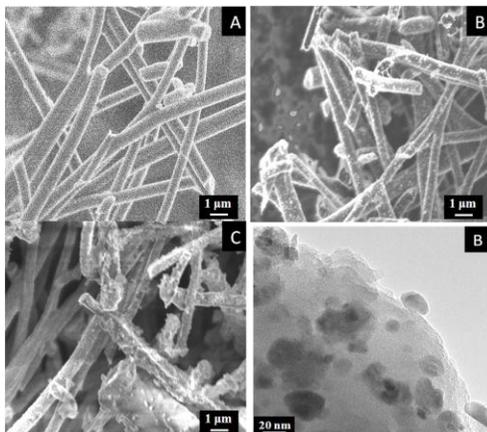


Fig.1. SEM images of MnOx impregnated PAN based activated carbon nanofiber ; (A) 0% MnOx, (B) 5% MnOx, (C) 20% MnOx

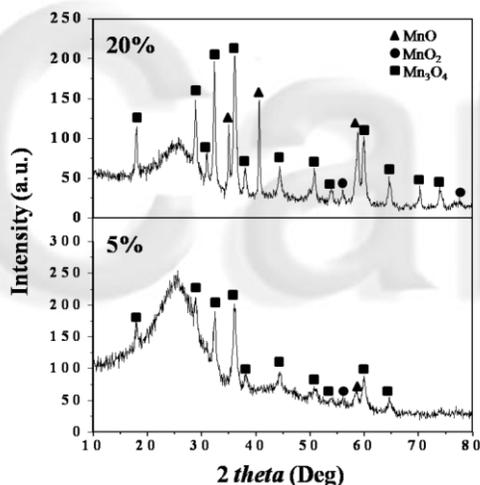


Fig. 2 XRD result of PAN based activated carbon nanofiber by MnOx contents 20% (up) and 5% (down)

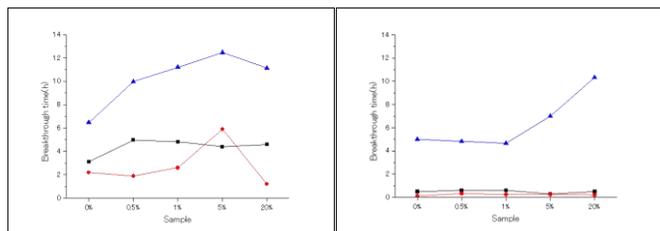


Fig. 3 and 4 Breakthrough time plot according to MnOx contents from 0% to 20% PAN ACNF(▲); FE100(■); FE300(●) in dry(Left) and wet(Right) conditions

The breakthrough time of each sample was plotted according to their manganese oxide content. Breakthrough time was defined as the time at which the outlet concentration reaches 1ppm which is 5% of the total inlet concentration of effluent. At dry condition with relative humidity 0%, the plain PAN-based activated carbon fiber showed better adsorption performance towards the other two activated carbon fiber samples regardless of difference in their surface area and pore characteristics. Manganese oxide compounds raised the adsorption capacity in overall and it could be confirmed in all the samples. (Figure 3) The improvement was the most noticeable for PAN-based ACNFs. From 0.5% to 5%, the formaldehyde removal efficiency increased up to more than 100% with breakthrough time of 12.47hs. 20% of manganese oxide content brought the prolongation time a bit shorter at 11.125hs but still maintained its superiority against the activated carbon nanofiber sample. FE100 sample also showed clear signs of improvement with manganese oxide compounds. From 0.5 to 20% ranges, the sample's removal performance improved however, the rate was not up to that of PAN-based activated carbon nanofiber samples. The removal performance under humid condition showed comparatively shorter breakthrough times (Figure 4). Commercial activated carbon fibers displayed a more significant performance drop of less than 1hr of breakthrough time. Regardless of manganese oxide content, the breakthrough time was reached in less than an hour in all commercial activated carbon fibers of FE100 and FE300. Activated carbon nanofiber, on the other hand, presented only a comparatively shorter breakthrough time, consistent adsorption and removal capacity. 5% of manganese oxide showed the most effectiveness on the activated carbon nanofiber support and 20% showed a little bit downward but still being longer than 0~1% samples. It was believed that some pore structures were blocked by heavy dose of coagulated manganese oxide particles that active sites connected from the surface were either blocked or futile. At both dry and humid condition, MnO_2 and Mn_3O_4 particles were tested without carbonaceous support by the same amount of 50mg and breakthrough time was always within 1h.

Conclusion

The novel concept of manganese oxide impregnated PAN-based activated carbon nanofiber catalyst was successfully synthesized with a seemingly few foibles in respect of particle size and dispersion. Since most of the manganese oxide catalyst were confirmed majorly to be hausmannite(Mn_3O_4), other forms of oxidative state need to be covered in the next line of study.

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