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Polyacrylonitrile/magnesium oxide-based activated carbon nanofibers with well-developed microporous structure and their adsorption performance for methane

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ABSTRACT

PAN-based ACNFs incorporated with MgO was prepared by electrospinning process followed by appropriate activation process. The addition of MgO caused physicochemical changes in term of smaller fiber diameter with an average diameter of 520 nm and higher surface area which is up to four times (1893 $m^2 g^{-1}$) as compared to pristine ACNFs (478 $m^2 g^{-1}$). Moreover, the modified ACNFs possessed a better adsorption capacity with higher CH_4 adsorption of 2.37 mmol g^{-1}. From the experimental data, the adsorption of CH_4 by composite ACNFs obeyed the pseudo-second order kinetic model with R^2 value up to 0.9996 and best fitted by Freundlich isotherm model.

Introduction

There are various porous carbon-based adsorbents have been utilized for methane storage such granular or powdered activated carbon (AC), activated carbon nanofibers (ACNFs), carbon nanotubes (CNT), and zeolites [1]. ACNFs have been widely used as adsorbent materials due to their smaller fibers diameter, highly porous structure, and high specific surface area [2]. In brief, ACNFs can be developed by carbonizing and activating the electrospun NFs at optimum temperature and conditions. As various precursors such as lignin [3], pitch [4], polymers [5], and synthetic precursors could be used to develop ACNFs, PAN-based ACNFs have become as an attractive alternative ascribed by its higher adsorption–desorption kinetics, low resistance to bulk flow, high strength, and heat stability [6].

In general, there are various available techniques in fabricating the nanofibers (NFs) based polyacrylonitrile (PAN) such as phase separation, template synthesis, self-assembly, and many more [7]; however, electrospinning process seems to be preferable as the process produces smaller diameter with uniform distribution of nanofiber structures [8]. Moreover, electrospinning offers more advantages than other techniques such as versatility, efficiency, and feasibility for mass production [9,10]. Recently, NFs in activated form have been developed to improvise the structures of NFs which creates abundant number of macropores and micropores structures, smaller fiber diameter, and greater specific surface area [11]. With those enhanced characteristics, ACNFs have greatly attracted many interests to be used for various applications, especially for gas storage. In addition, incorporation of some additives (nanoparticles or inorganic salts) into NFs has been proven to enhance the structures of the NFs [12]. It is believed that incorporating inorganic materials into NFs will allow a unique blend of properties including high heat stability, good mechanical strength, excellent moldability and flexibility of polymers, and at the same time maintaining the other functional properties of either constituent. Metal oxide nanoparticles such as magnesium oxide (MgO), manganese oxide (MnO_2), zinc oxide (ZnO) and nickel

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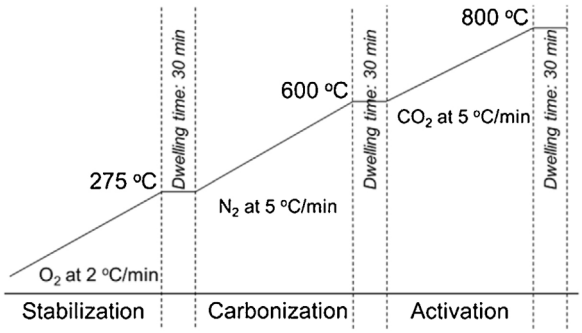

Fig. 1. Three stages of pyrolysis process of nanofibers.

oxide (NiO) have been profound to be as excellent candidates which enhance the physicochemical properties of polymer based ACNFs. These nanoparticles themselves are high in surface area and the additional of right amount of these nanoparticles into the nanofibers solution could improve their structure and adsorption capabilities [13,14].

Regardless their enhanced characteristics and advantages, there are only a few studies have been conducted on incorporation of metal oxide with ACNFs. Herein, in this current research, efforts have been focused on the fabrication, physicochemical properties and methane adsorption by PAN-based ACNFs incorporated with MgO. This new adsorbent material could contribute to the enhancement of more economic and safer alternative storage method for high volumetric methane.

Materials and methods

Fabrication and activation of nanofibers

Polyacrylonitrile (PAN), dimethylformamide (DMF), and magnesium oxide (MgO) nanoparticles were purchased from Sigma–Aldrich and used without any further purification. The pristine nanofiber mats (NFs) and NFs embedded with 15% of MgO (relative to PAN wt.) were fabricated via lab-scale electrospinning machine (Electroris®). Both resultant NFs was further stabilized under pure air of 200 ml min^{-1} at heating rate of 2 °C min^{-1} at 275 °C. The NFs were later carbonized at 600 °C under nitrogen flow at heating rate of 5 °C min^{-1} to produce carbon nanofibers (CNFs). The CNFs were physically activated in horizontal tube furnace (Carbolite CTF 12/65/550) at temperature of 800 °C under carbon dioxide flow at heating rate of 5 °C min^{-1} to yield activated carbon nanofibers (ACNFs) [15]. The overall pyrolysis process of the NFs is shown in Fig. 1.

Characterizations

The textural parameters of the ACNFs were determined from the N_2 adsorption–desorption isotherms at 77 K by Micromeritics ASAP 2000 while the crytallographical behaviors and carbonaceous properties of the ACNFs have been identified by using X-ray diffraction analysis (Bruker D8 Advance diffractometer) and Raman spectra analysis (RMP-510), respectively. The morphological and diameter of resultant ACNFs were characterized by using field emission scanning electron microscopy analysis while the elemental composition of resultant ACNFs were analyzed by using electron dispersive X-ray (EDX-HITACHI TM3000). At high magnification, the intrinsic structures of the resultant ACNFs were observed under transmission electron microscope (TEM). A simple static volumetric measurement method has been used for methane adsorption test and the ACNFs were regenerated via thermal swing method and followed by purging with an inert gas [16].

Kinetic studies and adsorption isotherms

The kinetic adsorption model of resultant ACNFs were simulated by the pseudo-first order and pseudo-second order kinetic models by plotting graphs of ln(qe – qt) against t, $\frac{t}{q_t}$ versus t and q_t against lnt, respectively. The differential (Eq. (1)) and integral forms (Eq. (2)) of the pseudo-first order model can be written respectively as [17–19]:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (1)$$

$$\ln(q_e - q_t) = \ln q_e - kt \quad (2)$$

where k_1 (g/mg h) is the adsorption rate constant for the pseudo-first order equation, q_e is the amount of CH_4 adsorbed at equilibrium (mg/g), and q_t is the amount of CH_4 adsorbed at any time (mg/g).

The differential and integral forms (Eqs. (3) and (4)) of the pseudo-second order model can be written respectively as:

$$\frac{dq_t}{dt} = k_1(q_e - q_t)^2 \quad (3)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} - \frac{t}{q_e} \quad (4)$$

where k_2 (g/mg h) is the adsorption rate constant for the pseudo-second order equation [20].

Results and discussions

Textural property

It is noteworthy to mention that a large amount of volatile compounds were eliminated during pyrolysis process which eventually resulted to the creation of new micropores that would increases the surface area of the nanofibers (NFs). As an outcome, the pores contributed to larger specific surface area (SSA) [21]. Eventually, the use of metal oxide which dissociates during heat treatment can as well increase the SSA and thus improving the rate of adsorption. Table 1 depicts the variation of SSA, micropore volume, pore size, and total pore volume (TPV) of pure ACNFs and ACNF MgO. It shown the SSA and micropore volumes of ACNF MgO are significantly higher than pure ACNFs and the addition of MgO led to an increase of micropores volume and widening of micropore sizes. In this study, as the MgO particles were introduced into the NFs, no beads were detected blocking the pores and resulting in ACNFs with small diameter and high SSA

Table 1
Textural properties of pristine ACNFs and ACNFs embedded with MgO.

Samples	BET S.S.A. (m^2/g)	Pore size (cm^3/g)	T.P.V. (cm^3/g)	V_{micro} (cm^3/g)	V_{meso} (cm^3/g)
ACNF	478	0.1938	0.2097	0.1593	0.0504
ACNF MgO	1893	0.7336	0.6212	0.5340	0.0872