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Research paper

Experimental investigation on the ammonia adsorption and heat transfer characteristics of the packed multi-walled carbon nanotubes

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HIGHLIGHTS

- Adsorption performance of ammonia on packed MWCNTs was studied.
- Effects of working pressure and temperature on the adsorption capacity were investigated.
- Adsorption equilibrium data and kinetics of ammonia on MWCNTs were analyzed.
- Equilibrium adsorption amount of ammonia varied 22.69–90.05 mg/g_{CNT} at different temperatures and pressures.

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ABSTRACT

Carbon nanotube (CNT) is considered as a kind of potential adsorbent because of its large surface area, uniform micropores and unique physicochemical properties. The adsorption performance of ammonia on the packed multi-walled carbon nanotubes (MWCNTs) were studied in this paper. Firstly, the packed MWCNTs were characterized by the scanning electron microscope (SEM) and transmission electron microscopy (TEM). Secondly, the effect of working pressure and adsorbent temperature on the adsorption capacity of ammonia by the packed MWCNTs was investigated. Thirdly, Langmuir and Freundlich models were used to analyze the equilibrium adsorption data and the adsorption kinetics was also discussed using a classical gas diffusion model. The Freundlich isotherm model could elucidate well the adsorption of ammonia on the MWCNTs when compared to the Langmuir equation. The research results showed that the equilibrium adsorption amount of ammonia by the MWCNTs varied between 22.69 and 90.05 mg/g_{CNT} at the adsorbent temperature of 25–35 °C and working pressure of 0.368–0.744 MPa. It seems that the pure MWCNT is not appropriate to act as the adsorbent for the solid–gas adsorption refrigeration due to its low adsorption capacity. However, our research indicates that the MWCNTs can be used as additive to some other chemical adsorbents to improve their heat transfer characteristics.

1. Introduction

Carbon nanotubes (CNTs) have attracted considerable attentions due to their unique structure, mechanical, and physicochemical properties since they were discovery by Iijima in 1991 [1–5]. CNTs are considered as one kind of potential adsorbents because of their large specific surface area, surface properties, hollow and layered structures and short adsorption equilibrium time [6,7]. According to the graphitic layer, the carbon nanotubes include two categories: single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs). Microporous nature of SWCNTs is distinct from the mesoporous MWCNTs according to the examination by Inoue et al. [8,9]. For diverse reasons, the adsorption behavior of CNTs has been extensively studied in the past decade [10]. CNTs exhibit the great potential for gas adsorption as a new adsorbent. The research of gas adsorption on CNTs can not only determine the morphology of CNTs but also evaluate their potential application. The adsorption capacity of gas via CNTs is mainly attributed to the pore structure and the large specific surface areas. Numerous researches have been conducted on the adsorption of gases and vapors in CNTs [11–13].

Much attention has been devoted to the potential applications of CNTs. As a promising clean energy, hydrogen is an alternative substitute for fossil fuels. Similar to activated carbons and carbon

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nanofibers, CNTs have drew extensive attention as potential hydrogen storage materials [14]. In the beginning, both theoretical predictions and experimental researches on hydrogen storage are extremely optimistic. The subsequent studies of the adsorption of hydrogen by CNTs produced a magnitude of conflicting results. The very low hydrogen storage capacity of CNTs started to emerge [15]. Some results of rather high hydrogen storage capacity were later manifested deriving from the faults of experiment [16]. In particular, the reports of possible room temperature hydrogen storage capacity arose some controversy [17]. The hydrogen storage capacity of pure CNTs is low and mutates widely in different studies. These researches have indicated that the physical adsorption hydrogen storage on pure CNTs may not be a feasible method. However, lots of researches are still ongoing.

Ammonia (NH_3) is a common gas and has been widely investigated on adsorption for numerous purposes. Dipendu and Shuguang [11] measured and compared the adsorption properties of carbon dioxide, methane, nitrous oxide, and ammonia on the ordered mesoporous carbon. Mark et al. [12] studied the adsorption of ammonia and nitrogen dioxide on SWCNTs. Ammonia could be adsorbed at room temperature via both the lone pair and the H atoms. Bahram et al. [13] carried out the theoretical investigation to characterize the behavior of ammonia molecules adsorption on external surface adsorption on the (5,0), (8,0), (5,5) and (6,6) SWCNTs via the DFT(density functional theory) calculations. The research results showed that the equilibrium tube-ammonia distance was very sensitivity to the type of tubes. In addition, Bahram et al. [18] performed the theoretical study of $NH_3(H_2O)_n$ ($n = 0,1,2,3$) complex adsorption on (8, 0) SWCNTs. Even so, the progress made seems to lag behind what was expected. CNTs could efficiently remove trace concentrations of toxic air pollutants and have rapid adsorption kinetics for removal of hazardous substance [19]. The ammonia is of very importance in industry but a major pollutant that needs to be removed from many industrial gas streams [11]. Much attention has been paid to detect the ammonia using CNTs as sensors and few studies focused on the adsorption characteristic of ammonia on MWCNTs. The current data available are not enough to acquire the adsorption performance and adsorption rate of ammonia onto the MWCNTs. Hence, it is a desirable work to investigate the kinetics equilibrium and thermodynamics of the adsorption of ammonia on the MWCNTs.

Solid-gas adsorption refrigeration has a series of advantages over the mechanical vapor compression refrigeration due to easier control, no vibration and lower operation costs [20]. Adsorption refrigeration is an environmentally friendly refrigeration technology for the reason of the utilization of natural working medium, and it can be driven by low-grade energy (such as solar energy, waste heat). Ammonia is commonly employed as a refrigerant in the adsorption refrigeration using activated carbon and metal chlorides as adsorbents. Among these adsorbents, activated carbon is a physical adsorbent, whereas the metal chlorides are the chemical adsorbents. As for the popular physical adsorbent, activated carbon has the higher adsorption capacity of ammonia. However, the thermal conductivity of the activated carbon is relatively low. The enhancement of heat and mass transfer plays a very important role in improving the system COP (coefficient of performance) for the adsorption refrigeration system [21]. On the other hand, metal chlorides might confront with the swell and agglomeration during the chemical adsorption processes [22,23]. These phenomena would cause the deterioration of adsorption capacity after many reduplicative cycles and thereby become the obstacles to prevent these systems from widespread utilization. Similarly, there exists the problem of the poor heat transfer. Expanded natural graphite (ENG) has been widely utilized as the matrix to intensify the heat transfer of adsorbents [24]. ENG can also improve the mass transfer performance for the chemical adsorbents due to the rich porous structure. Meanwhile, it can prevent the swelling, disintegration and agglomeration for the chemical adsorbents. However, it can hardly contribute to improve the adsorption capacity of ammonia according to the experimental investigation performed by Li et al. [25]. It was well known that the CNTs exhibited the prominent heat and mass transfer characteristic because of the high thermal conductivity, the hollow geometry and porous structure. Thus, it infers that CNT is a possible kind of adsorbent for solid–gas adsorption refrigeration using CNTs-ammonia working pair. The aim of this work is to investigate the adsorption capacity and adsorption rate of ammonia on the CNTs, and the thermal transport properties of CNTs composite adsorbents. The scanning electron microscope (SEM) and transmission electron microscopy (TEM) are firstly used to study the morphology of the CNTs and then the adsorption performance of ammonia on the CNTs is measured using a magnetic suspension balance. The Freundlich isotherm model is applied to fit the experimental data, and the adsorption kinetics of ammonia on the CNTs is also conducted and discussed by applying the classical diffusion model. Besides, the thermal conductivity measurement of CNTs composites has been performed.

2. Materials and methods

2.1. Materials

The CNTs adopted herein are multi-walled carbon nanotubes, which are utilized without further purification. The samples of pristine MWCNTs are manufactured by the Nanjing Jcnano technology Co., LTD (China). The purity of MWCNT is higher than 95%, with the remaining part being catalyst residues. The average diameter and the length of MWCNTs are 11 nm and 10,000 nm, respectively. The surface area of MWCNTs is higher than 200 m^2/g. Both morphology and crystal structure of pristine MWCNTs were observed by SEM and TEM. SEM measurement is carried out on the FEI Sirion 200 at an accelerating voltage of 5 kV. TEM measurement is conducted on the FEI Tecnai G2 Spirit Biotwin operated at an accelerating voltage of 120 kV. A SEM photo enlarged 2×10^5 times is shown in Fig. 1(a). Fig. 1(b) shows TEM photo of the pristine MWCNTs. It can be seen that the cylindrical MWCNTs form a wide meshed network and entangle with each other. Moreover, the MWCNTs are usually curved and form an aggregated structure due to the inter-molecular force. It can be seen the tubular microstructure of MWCNTs from these photos. The MWCNTs are not only aggregated but also entangled.

2.2. Experimental apparatus for testing equilibrium adsorption properties

In order to evaluate the ammonia adsorption capacity of MWCNTs, the adsorption capacity and adsorption isobar are measured using a Rubotherm magnetic suspension balance. The whole experimental test unit is composed of a Rubotherm magnetic suspension balance, a thermostatic glycol water bath, a thermostatic oil bath and a vacuum pump.

A pictorial view of the experimental rig is shown in Fig. 2, and its working principle of the whole system is shown in Fig. 3. The sample is placed in a small basket, which is hanged inside of the steel chamber via the load hook. The chamber is surrounded by a steel jacket. The oil circulates through into the jacket to control the temperature of the sample. The oil temperature is regulated and controlled through the thermostatic bath (Julabo SE-6). The resolution of this Julabo thermostatic bath is 0.01 °C. The ammonia container is immersed into the glycol water bath with the certain