Journal of Molecular Structure 1173 (2018) 792–800

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: http://www.elsevier.com/locate/molstruc

Enhancement of CO_2 adsorption on polyethylenimine functionalized multiwalled carbon nanotubes/Cd-nanozeolite composites

Samira Salehi, Mansoor Anbia*, Amir Hossein Hosseiny, Mohammad Sepehrian

Research Laboratory of Nanoporous Materials, Faculty of Chemistry, Iran University of Science and Technology, Farjam Street, Narmak, P.O. Box 16846-13114, Tehran, Iran

ARTICLE INFO

Article history:
Received 18 May 2018
Received in revised form
29 June 2018
Accepted 18 July 2018
Available online 19 July 2018

Keywords:
Nanozeolite
CO2 adsorption
Ion exchange
Polyethylenimine
Nanocomposite

ABSTRACT

In this study, to enhance the adsorption of carbon dioxide (CO_2), a nanozeolite (Nano-Z) was modified with Cu^{2+}, Ni^{2+}, Cd^{2+}, Mn^{2+} and Co^{2+} by cation-exchange method. The adsorption capacity of CO_2 in modified nanozeolites increases with increase in the meso-pore volume of Nano-Z through ion exchange by divalent cations with appropriate ion radius. The adsorption isotherms of CO_2 are investigated by employing a volumetric measurement at two temperatures (25 °C and 100 °C) and a pressure range up to 20 bar. The highest CO_2 adsorption was observed at both temperatures for Cd-exchanged Nano-Z. A hybrid composite of Cd-exchanged Nano-Z and amine modified multi-walled carbon nanotube (MWCNT) has been synthesized by hydrothermal method. Polyethylenimine (PEI) was chosen as the amine source in the preparation of amine-functionalized MWCNT. Amine functionalized Nano-Z/Cd exhibited improved adsorption capacity of CO_2 by combination of physical and chemical adsorption. Scanning electron microscopy (SEM), Energy Dispersive X-ray spectroscopy (EDX), X-Ray Diffraction (XRD), N_2 adsorption/desorption isotherms and Fourier Transform Infrared (FT–IR) were used to characterize the resulting nanocomposites.

1. Introduction

The rise in the levels of atmospheric concentration of carbon dioxide (CO_2) has contributed to global warming, currently one of the greatest threats to human life and the environment [1]. In reality, as far as the Industrial Revolution, CO_2 concentration in the atmosphere has increased rapidly and continues to grow so far [2]. On the other hand, acid gases such as H_2S, CO_2 and SO_2 are in a variety of gas streams, including flue gas, synthesis gas and natural gas, refinery gases [3]. Presence of acidic gas in natural gas streams leads to several serious problems such as reduction of natural gas heating value and pipeline capacity and equipment and pipeline steels corrosion [4].

Thus CO_2 capture and separation have been receiving significant attention [5]. Moreover, commercial CO_2 capture technology has been very expensive and energy intensive [6]. Many gas separation tasks need more environmentally and economically new effective sequestration processes [7]. It is also important to note that CO_2 is an abundant, non-toxic, economical, and recyclable carbon source. Thus, the utilization and conversion of CO_2 have attracted extensively attention in the whole world. Technologies such as absorption, membrane, cryogenic distillation and adsorption have been used to date for the capture and separation of CO_2 from the different sources.

The absorption with amine solution is still most widely used for CO_2 capture due to its high selectivity. However, this operation has important drawbacks: corrosion in the presence of O_2 and other impurities, high solvent degradation rates because of its reaction with NOx and SO_2 and the large amounts of energy needed for regeneration [8]. Membrane separation is also limited to the low separation efficiency and it is hard to realize industrialization [9].

The adsorption method, which is used for capturing CO_2, has shown great promise, due to its low energy requirements, cost advantage, and ease of applicability over a relatively broad range of temperatures and pressures [10]. Recently, extensive research activities have been focused on the progress of technologies based on adsorption of CO_2 on carbon nanotubes (CNTs) [11], zeolites [12], metal–organic frameworks (MOFs) [13], mesoporous silica materials [14] and activated carbons (ACs) [15].

Zeolites show some advantages as porous solid adsorbents such as a high adsorption capacity and selectivity, more stable at high

* Corresponding author.
E-mail address: anbia@iust.ac.ir (M. Anbia).

https://doi.org/10.1016/j.molstruc.2018.07.056
0022-2860/

temperatures than other materials, large surface area and more active sites on the surface to adsorb CO_2 [16,17]. In addition, other materials such as mesoporous silicas and metal–organic frameworks are not commercially available yet and targeted CO_2 separation costs can make their application uneconomical in the near future, but zeolites are inexpensive and easily available [18].

Zeolites are microporous, crystalline and hydrated aluminosilicates of inorganic cations (alkali or alkaline earth cations) that possess a 3D framework structure [19,20]. The zeolite framework consists of an assemblage of alumina (AlO_4) and silica (SiO_4) tetrahedra joined together in various regular arrangements through shared oxygen atoms to create an open crystal structure containing pores of molecular dimensions in to which guest molecules can penetrate [21]. Although their chemical composition is limited to aluminosilicate tetrahedra, cations should be introduced to compensate the negative charge of oxygen connected to Al atoms in the framework [22]. This chemical versatility allows for the modification of some physicochemical zeolite properties (such as hydrophilic– hydrophobic nature, acidity or redox properties) and, consequently, tunes them for a specific application [23,24].

To improve CO_2 adsorption capacity, cations in the framework can be replaced by other cations in many ways [25]. Ion exchange by divalent cations with appropriate ion radius can increase the meso-pore volume of adsorbents, thereby increasing the adsorption capacity for CO_2 [26].

Zeolite beta was modified with alkali and alkaline earth metal ions and zeolite K-beta has shown the best adsorption capacity [27]. Adsorption and selectivity of CO_2 over N_2 by cation exchanged zeolite L have been investigated and zeolite-CaL reveals incredibly high CO_2 selectivity over N_2 [28]. Zeolite Y and zeolite X were modified by alkali metal cations and the experimental results have shown that the largest CO_2 capacities for materials containing the small Li cations [29].

Recently, a number of studies have been conducted focusing on the preparation of mesoporous-based composite materials for the improvement of CO_2 adsorption capacity. Composites are made from a combination of two or more materials whose individual properties differ from one another, resulting in the formation of a synergetic effect [30].

The most of the zeolites tend to experience a dramatic drop in their adsorption in their adsorption capacity when exposed to moisture. Indeed, the introduction of H_2O repellent components such as multi-wall carbon nanotubes (MWCNTs) could improve the hydrophobic property of zeolites. MWCNTs applied as composite fillers, have been investigated for different applications and increased composite performance has been achieved [31]. We suggest a strategy to improve the adsorption capacity of the original material by adding MWCNTs. Intermixing MWCNTs with Nano-Zs lead to appearance of unique physical and chemical properties viz. good dispersibility and high pore volume, which is associated with increasing rapidity of adsorption.

Porous solid adsorbents including a supported polymeric amine can have rapidly adsorption and desorption cycles, high sorption capacities and low energy consumption [32]. CO_2 is acidic, thus the introduction of basic amine into Nano/Z can promote the interaction between CO_2 molecules and adsorbent [33]. Among various porous solid adsorbent supports, polyethyleneimine (PEI) impregnation on porous solid to the preparation of amine-functionalized adsorbents have been attracting great attention due to its easy preparation procedure which can be simply translated to commercial scale. In addition, PEI has more amine groups per molecule than other amine-containing compounds.

In this study to increase the adsorption capacity of CO_2, Nano-Z has been modified with Cu^{2+}, Mn^{2+}, Ni^{2+}, Co^{2+} and Cd^{2+} and the effect of ion exchange has been studied. The adsorption isotherms of CO_2 on the zeolitic adsorbents were measured at 25 °C and 100 °C and with a pressure range of 0–20 bar by means of the volumetric adsorption method. The novel zeolitic nanocomposites were prepared by functionalization MWCNT by PEI and adding to the Cd-exchanged Nano-Z. The zeolitic samples before and after functionalization were characterized by SEM, EDX, XRD, N_2 adsorption/desorption isotherms and FT–IR.

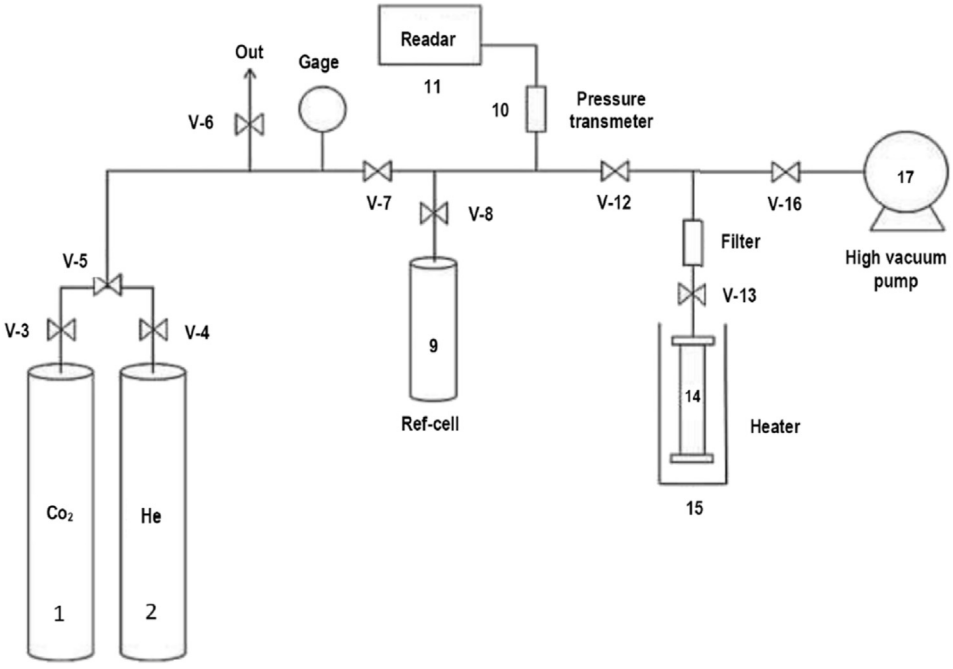

Fig. 1. Setup for adsorption capacity test.