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Removal of the CO_2 from flue gas utilizing hybrid composite adsorbent MIL-53(Al)/GNP metal-organic framework

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ABSTRACT

In this study, adsorption of the CO_2 and N_2 gases on the MIL-53(Al) and its hybrid composite with the graphene nano-plates (GNP), MIL-53(Al)/GNP, adsorbents were investigated. These materials were synthesized using the solvothermal reaction method. The prepared samples were characterized by means of the powder X-ray diffraction (PXRD), field emission scanning electron microscopy (FESEM), N_2 adsorption–desorption isotherms (BET-BJH surface area measurement) and Fourier transfer infrared (FT-IR) spectroscopy methods as well as; thermogravimetric analysis (TGA). Adsorption equilibrium of the CO_2 and N_2 on the sorbents were determined through a volumetric adsorption apparatus at 298, 323 and 348 K and pressures of up to 40 bars. It was found that, the adsorption capacities of the CO_2 on the MIL-53(Al)/GNP containing 5 wt% GNP increased about 35% (from 9.61 to 12.95 mmol gr^{-1}) in comparison with that of the GNP free sample at 298 K and 40 bars. This enhancement in the adsorption capacity was attributed to the incorporation effect of the GNP displayed in terms of the increase of the specific surface area (S_{BET}), internal pore volume (V_p) and micropore volume (V_{micro}) of the MIL-53(Al). Finally, several dual sites isotherm models including the; Langmuir, Sips and Toth were utilized to fit the obtained adsorption experimental data trying to describe the observed breathing effect. In this venue, the ΔH_{ads} was calculated in order to predict the thermodynamic behaviors of this MIL sorbent due to adsorption of the CO_2.

1. Introduction

In the recent decades, concentration of the CO_2, CH_4 and other greenhouse gases significantly risen in the atmosphere leading to destructive consequences such as the climate change, melting of polar ices etc. [1,2]. Therefore, it was considered to be an urgent subject matter to find out suitable and viable operative techniques towards emission prevention of the greenhouse gases into the environment. Amongst these gases, CO_2 recognized as one of the most important species formed as a main product of the combustion processes. As a major source of the CO_2 emission, flue gas streams considered to be a worthy candidate [3,4]. Hence, design and development of appropriate CO_2 capture processes attracted a lot of scientific attentions. One of the most popular processes for CO_2 removal from different gaseous mixture streams considered to be the gas absorption technique through which the amine-based solvents played a major role and traditional aqueous mono-ethanol-amine most extensively used as scrubbing agent [5]. However, amine based systems for the CO_2 capture incorporated some complications including their; high energy requirement for regeneration, toxic nature and corrosion problems [5,6]. Thus, alternative processes for the CO_2 capture via adsorption on porous solid materials were sought. In this venue, activated carbons [7,8] and zeolites [9,10] were inquired extensively and amongst them, metal organic frameworks (MOFs) received higher attentions as novel crystalline solid materials for diverse applications [10,11]. Their rather large pore sizes labeled these species as a new class of porous media crystalline solids. In the past 15 years, the scientific society observed significant progresses in the design, synthesis, and characterization of various metal-organic frameworks owning to their tremendous textural, structural and chemical diversity [10–12]. Moreover, these materials well known for their potential applications in the gas adsorption and storage [13], molecular separation [14], ion exchange [15] and heterogeneous catalysis [16] fields. The MOF materials made of combination of two major components as building blocks including; a metal ion or cluster of

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self-assembled metal ions and an organic molecule named ligand [10–16]. The organic elements were typically di-, tri-, or tetravalent linkers. This combination of the two components provided infinite potentials. In other words, very large varieties of the MOFs structures might have been counted for as results of possible collaborations between metal clusters and organic ligands. The essential scheme relied upon use of the metal ions having multiple coordination sites and multidentate ligands (organic linkers) capable of playing roles as bridges between two or more metal clusters and interconnect them to each other at a time [10–12,14,16]. Appropriate choices of the metal atoms and organic linkers considered to be the main key to synthesize the MOFs containing adjustable pore size, pore volume and other textural and structural properties. Moreover, the most remarkable differences of these with the traditional inorganic materials known to be their extraordinary high porosity (of up to 90%) as well as huge specific surface areas some extended beyond 6000 $m^2 g^{-1}$ [17].

Although most MOFs were known as rigid solid materials, some of the recent studies showed that, single component isotherms of the CO_2 upon them differed considerably when this species adsorbed on a group of iso-typical crystalline porous terephthalates [18]. In other words, in contrast with other solid-state materials such as; zeolites, activated carbons and metal oxides, a number of MOFs recognized to exhibit high skeleton flexibility and reversible shrinkage/expansion processes due to their interaction with some adsorbed molecules [19].

Ferey et al. [20] synthesized chromium terephthalate based MIL-101 with pores in meso size range of ~3–4 nm and internal specific surface area extended beyond 3900 $m^2 g^{-1}$. Serre et al. [21] synthesized the first Cr (III) dicarboxylate MIL-53 using hydrothermal reaction method under medium conditions belonging to the class of MIL-n series materials. The MIL-53 existed in two forms including the; low-temperature ones filled with guest molecules and high temperature species as guest free solids. The transition process between these forms was fully reversible and followed by a very high breathing effect, whereby the structures interchanged between the two narrow-pore (np) and large-pore (lp) forms; respectively [18,21]. Similar breathing occurred when the Cr atom was exchanged with other metal atoms such as the; Al, Fe and Ga. This was related to the existence of the —OH functional groups in 1-D tunnels intensely interacting with polar guest molecules [21–23]. However, such intense breathing effect didn't occur for the vanadium kind of the MIL-47 material, where there were no —OH groups in the framework [24].

The MIL-53(Al) formed due to the dicarboxylate groups of the terephthalate units playing role as ligands to interconnect infinite chains of corner-sharing $Al_4(OH)_2$ octahedral inorganic clusters to each other [22]. Such corporations between metal clusters and organic bridges resulted in 1-D long diamond-shaped channels [21–24].

Despite of the hydrophobic nature of the organic walls of the MIL-53(Al) pores, the reversible adsorption of one water molecule per Al atom at ambient temperature changes the MIL-53(Al) structure from (ht) to (lt) form and involves a noteworthy variation of the dimensions of the internal pores from (8.5×8.5 Å^2) to (2.6×13.6 Å^2), respectively, due to the establishment of a pair of hydrogen bonds between water and the hydrophilic unit of the framework (metal clusters) [22]. This transition between the two forms is completely reversible and followed by a very intensive breathing effect. Therefore, it can be concluded that, the structure of MIL-53(Al) in the presence of the water molecules is stable and no collapse and/or distortion of the framework occurs.

On the other hand, the breathing effect attributed to the electrostatic interactions between quadruple moment of the CO_2 molecules and —OH groups led to a large amount of this species (*i.e.*; CO_2) being adsorbed on the MIL-53(Al). Efforts also made to utilize suitable promoters to improve the MOFs adsorption performance resulted in an alloy-like porous solids called a hybrid composite adsorbent. Appropriate adsorbents for the CO_2 capture ought to satisfy two major criteria including possessing; i) a highly porous medium capable of adsorbing and storing large amounts of the CO_2 molecules (due to suitable textural and structural properties) and ii) well-developed chemical properties (by the presence of functional groups as promoters) in order to confirm reactive adsorption process [25]. More specifically, the pore size distribution of adsorbents should be in the micro range because under room conditions, CO_2 adsorbed and engaged only in pores similar to its kinetic diameter [26]. Furthermore, the main consequences of existence of reactive-adsorption sites appeared in forms of; i) strong adsorption interactions (*i.e.*; high affinity), ii) chemical transformations (*i.e.*; mass transfer and reaction) and/or iii) larger selectivity due to the adsorption. All of these were significant features of the gas purification, separation and catalytic processes [25,26]. This reactive adsorption might be achieved through presence of the functional groups and promoter materials on the adsorbent's internal surfaces to make a hybrid composite adsorbent. In other words, the large free volume of the MOFs' structure was not entirely utilized for gas storage because of the weak interactions between internal walls of the framework and typically small adsorptive gas molecules as well as; low density of the frameworks [27]. In order to make efficient use of the MOFs' available void space, other microporous or layered structures incorporated and/or embedded as promoter components resulting in uniformly distributed strong dispersive forces.

Yaghi et al. [28] found IRMOF-6 to have a large adsorption capacity of CH_4 due to the suitable size and structure of its pores. After this detection, other MOFs have been established and considered for utilizing as novel CO_2 adsorbents or storage medium, by optimizing the pore size and structure for the CO_2 molecule. Yaghi et al. [11] also investigated the CO_2 capacities of nine MOF materials. Chen et al. [29] examined using of MOF-508b, a MOF with 1-D micropores for the separation of CO_2 from N_2 and CH_4 mixture. Ferey et al. [30] studied CO_2 capture process with MIL-53 ($M = Al3^+, Cr3^+$), that formed a framework of 1-D long-diamond shaped pores with internal diameters of about 8.5 Å. Kaneko et al. [31] investigated the CO_2 adsorption performance and properties of $[Cu(bpy)(BF_4)_2(H_2O)_2\cdot(bpy)]$, that exists in 2-D plates form. These plates offset from each other by hydrogen bonding that each unit cell involved individual micropores. Kaneko et al. [32] also examined $[Er_2(PDA)_3(H_2O)]\cdot 2H_2O$ (PDA = 1,4-phenylendiacetic acid)], that adsorbed CO_2 molecules upon its internal activated surfaces. Snurr et al. [33] performed CO_2 equilibrium adsorption studies on $Zn_2(NDC)_2(DPNI)$, whose mixed organic units (ligands) formed 3-D rectangular frameworks. Snurr et al. [33] also studied the CO_2 adsorption performance of MOF-5, IRMOF-3, and MOF-177. Thomas et al. [34] examined CO_2 capture process with $Ni_2(bpy)_3(NO_3)_4$ that involved 3-D channels between the bipyridine organic bridges. There have been many efforts to contain molecular functionalities in MOFs capable of chemical adsorption in order to improve adsorption performance and capacities of CO_2 at low partial pressures. Blom et al. [35] synthesized three MOFs by use of amine-modified BDC molecules as ligands. All three amine-modified MOFs showed smaller specific surface areas and pore spaces than their virgin counterparts.

Anbia et al. [36] incorporated multi walled carbon nanotubes (MWCNTs) into MIL-101 to synthesize a hybrid composite adsorbent and measured the CO_2 adsorption capacity at 298 K and up to 35 bars. They reported an enhancement in adsorption capacity of about 60% (from 0.84 to 1.35 mmol g^{-1}) at 298 K and 10 bars compared with the virgin MIL-101. Jasra et al. [37] incorporated