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Synthesis, characterization, and CO_2 breakthrough adsorption of a novel MWCNT/MIL-101(Cr) composite

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ABSTRACT

Carbon dioxide is quantitatively the most significant component which facilitates in the global warming, it is utmost necessary to suppress the rapid increase of CO_2 concentration in the atmosphere by means of Carbon Capture and Storage (CCS). Metal-organic framework (MOF) MOFs has recently been developed with the primary objective of CO_2 capture from flue gases with minimum energy penalties. MIL-101(Cr) holds the supreme importance amongst such types of MOFs owing to its extraordinary thermal and hydro stability. In this study, a novel composite composed of multi-walled carbon nanotubes (MWCNTs) incorporated in a MIL-101(Cr) framework has been synthesized using a molecular-level mixing process in order to enhance the thermal properties of the base framework as well as augment the CO_2 adsorption capacity and separation. The synthesized and activated MWCNT/MIL-101(Cr) composites have been characterized for degree of crystallinity, microstructure, thermal stability, and CO_2 and N_2 equilibrium adsorption capacity. Actual dynamic behavior of adsorption breakthrough tests have been conducted under ambient conditions (297 K and 101.325 kPa) to address the real adsorptive behavior and to quantify the level of the CO_2 adsorption capacity and breakpoint enhancements.

Results demonstrate that a substantial improvement in the CO_2 adsorption capacity and breakpoint over pristine MIL-101(Cr) is achievable with the 2 wt% MWCNT/MIL-101(Cr) composite with measured optimal enhancements of about 35.94% and 32.11%, respectively.

1. Introduction

In the recent decade, environmental pollution is being identified as the most significant factor in the context of environmental health and safety. In this scenario, the major portion of the environmental pollution arises from fossil fuel burning processes in the form of greenhouse gases, including carbon dioxide, nitrogen oxide, and methane. These gases play a continuous and a vital role in facilitating universal environmental hazards like global warming, shore floods, atmospheric heat waves, land droughts, and destruction of cold-marine life. Moreover, the continuous change in climatic conditions are also expected to reduce the world's gross domestic product by about 5–20% [1]. The increase of the atmospheric temperature was measured to be about 0.74% in the last century and is predicted to reach to about 6.4% at the end of the current century [1]. In this context, carbon dioxide holds the most significant proportion of the flue gases being released into the atmosphere from various sources [2]. Therefore, a considerable amount of effort has been made by scientists, institutions, countries, and environmental organizations to minimize and control the amount of CO_2 emission in the atmosphere. The main source of CO_2 emission are considered to be the fossil fuel combustion processes whereby the fossil fuel appears to be the most dominating and pollution-free source of electricity on a global scale and therefore plays a vital role for a comfortable and sustainable lifestyle. Therefore, the only currently available feasible solution to continue fossil fuel utilization to meet energy demands with minimized CO_2 emission is carbon capture and storage, with the secondary aim of mitigating the global climate change.

The on-going research in the field of Carbon Capture and Storage (CCS) is gaining momentum every day. A vast majority of researchers have already investigated CO_2 separation and storage, using both experimental and simulation methods, with the primary objective of developing novel adsorption materials or adsorbents for this purpose [3]. The foremost advantage of using adsorption as a means of CO_2 separation is the ease of regeneration of the adsorbent material by applying heat and/or decreasing the operating pressure [4]. Activated carbons and zeolites are currently the most commonly exploited adsorbents in the context of research based on CO_2 separation and storage.

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More specifically, zeolites have been researched to a larger extent than activated carbons for carbon capture and hydrogen storage in applications involving relatively lower operating pressures [5,6], whereas carbon based materials, including activated carbons, have been preferred over zeolites for high pressure applications [6,7]. However, the noticeable advantages of carbon-based materials over zeolite-based adsorbents include cost-effectiveness, stability towards exposure to water vapor, lower energy required for regeneration due to lower heat of adsorption, and ease of production on a commercial scale [8].

Polyethylenimine (PEI)-impregnated millimeter-sized mesoporous carbon spheres have been developed and studied for CO_2 post-combustion capture [9]. The maximum CO_2 uptake was measured to be about 163.4 mg/g at 0.15 bar and 75 °C, which however was observed to decline during the cyclic adsorption/desorption experiment. The advantage of zeolite-based adsorbents over activated carbons is the relatively higher CO_2 adsorption capacity, especially at lower adsorption pressures. However, the CO_2 uptake is greatly reduced in case of CO_2/H_2O mixture as and requires significantly higher regeneration energy [10,11].

A novel class of mesoporous materials have been discovered almost two decades ago which are referred to as metal-organic frameworks (MOFs) in accordance with an organic portion (linker) and an inorganic constituent (metal ion clusters) coexisting in the same structure [12]. In the context of CO_2 adsorption, MOF-2 appeared as the first candidate to be evaluated for CO_2 uptake as well as selectivity [12]. The highest CO_2 uptake was, however, reported for MOF-177 as 1470 mg/g at 35 bar [13]. In the subsequent years, a vast majority of MOFs have been synthesized by research communities worldwide with the aim of designing the most optimum framework topology in order to maximize the CO_2 uptake as well as selectivity simultaneously. More specifically, a total of about 54,341 MOFs designed for these applications have been recorded in the Cambridge Structure Database before July 2015 [14].

A certain class of MOFs incorporating functionalized and open metal sites have shown high separation efficiency at ambient pressure like HKUST-1, Mg-MOF-74 and NH_2MIL-53 (Al) [15]. With regards to maximum uptake, a few MOFs have shown a reasonably high CO_2 adsorption capacity such as CPM-5, MIL-53(Al), UMCM-150 and Ni-STA-12, while others have been evaluated for comparatively lower uptakes like MOF-5 and MOF-177 [15]. A nickel-based MOF, Ni/DOBDC, was also investigated for CO_2 capture and was measured to exhibit a fairly high adsorption capacity [16].

MIL-101(Cr) is a chromium(III) terephthalate and is characterized by a higher specific surface area as well as water-stability than a wide variety of MOFs reported in literature [17]. In addition, it has been reported to show a strong resistance towards contaminants contained in flue gases such as H_2O, NO and SO_2, a relatively lower energy required for regeneration, and ease of commercial production [17]. These features have helped to prioritize the use of MIL-101(Cr) as an attractive adsorbent material for CO_2 capture and storage [17]. A recent investigation aimed at improving the CO_2 uptake and separation efficiency of MIL-101(Cr) by incorporation of polyethyleneimine (PEI) in the framework resulting in PEI/MIL-101(Cr) composites. The results demonstrated a relatively lower adsorption capacity of CO_2 for PEI/MIL-101(Cr) composites compared to that measured for pristine MIL-101(Cr); however, the selectivity of CO_2 over N_2 was significantly improved [18]. Functionalizing Mg-DOBDC (MOF-74) with ethylene diamine (ED) improved both CO_2 adsorption capacity and recycling stability under low CO_2 partial pressures [19]. Supported Layered Double Hydroxides by Graphene Oxide exhibited an increase in the CO_2 adsorption capacity by about 60% more than the pure Layered Double Hydroxides [20]. N-doped zeolite-templated carbon could adsorb about 4.4 mmol/g of pure CO_2 at ambient conditions (1 bar and 298 K) [21]. Poly(allylamine)–silica composites showed a good capacity for CO_2 separation from flue gases and air [22]. Incorporating titanium with DMS-TN showed almost twice CO_2 adsorption capacity and more stability than those of pristine adsorbent (DMS-TN) [23].

Since the last one and a half decade, carbon nanotubes (CNTs) have also attracted a considerable attention of research groups engaged in carbon capture and sequestration in view of the chemical affinity exhibited by CNTs towards CO_2 uptake and selectivity [24–28]. More specifically, the attachment of amino- functionalities to the sidewalls of CNTs has resulted in a considerable enhancement in the intrinsic CO_2 adsorption capacity measured for CNTs [29–32]. Su et. al [33] have studied the effect of functionalization of CNTs with 3-aminopropyltriethoxysilane (APTES) groups on the CO_2 uptake and selectivity. They found that the co-existence of moisture increased the CO_2 adsorption capacity measured for APTES-functionalized CNTs. The CO_2 adsorption capacity was measured to be about 2.59 mol/kg at 293 K for APTES-functionalized CNTs which clearly confirms functionalization to be an effective tool for improving the intrinsic CO_2 adsorption potential of CNTs. Incorporating CNT and lithium ions with MOF $Cu_3(btc)_2$ resulted in improving the CO_2 capacity by about 305% compared with those of the base adsorbent ($Cu_3(btc)_2$) [34]. Also, the adsorption capacity of CO_2 at high pressure and room temperature (10 bar and 298 K) was improved by adding MWCNT to MIL101 [35].

A considerable number of research attempts based on CO_2 capture and separation have been conducted so far in terms of breakthrough, pressure swing adsorption and temperature swing adsorption which include both experimental method and numerically validated simulations [36–50]. The maximum amount of research focus has, however, been invested on the lab-scale development of novel adsorbent materials designed for achieving high CO_2 capture capacity as well as selectivity. In this context, the poor thermal conductivity exhibited by a vast majority of these newly-synthesized adsorbents has been experienced as a major obstacle in improving the CO_2 capture capacity of these materials. More specifically, a very limited number of research attempts have focused on the improvement of CO_2 capture and/or separation *via* improving the thermal properties of the base adsorbent. In this context, the current study aims at investigating the effects of incorporating multi-walled carbon nanotubes (MWCNTs) inside MIL-101(Cr) with the aim of improving the thermal properties of the framework and investigating the influence of MWCNT addition on the CO_2 uptake and adsorption breakpoint of the resulting MWCNT/MIL-101(Cr) composites. The synthesized and activated MWCNT/MIL-101(Cr) composites have been characterized for degree of crystallinity, microstructure, thermal stability, CO_2 adsorption isotherms, and CO_2 breakthrough characteristics. The effects of MWCNT addition on the CO_2 uptake and breakthrough capacity have been documented, and the most favorable proportion of MWCNTs inside MIL-101(Cr) resulting in the most optimum combination of these two characteristics has been proposed.

2. Experimental work methodology

For the synthesis of MIL-101(Cr), the method proposed by Férey et al. [51] has been adopted. Briefly, 4 g chromium nitrate nonahydrate ($Cr(NO_3)_3.9H_2O$), 1.66 g 1,3 benzenedicarboxylic acid (BDC) and 47.4 ml de-ionized water were added to a 125 ml Teflon-liner which was sealed inside a stainless steel autoclave and kept at 220 °C for 8 h. The autoclave was cooled slowly to room temperature, after which the light green solid was recovered using centrifugation at 8000 RPM for 45 min. In order to remove the guest molecules, the as-synthesized MIL-101(Cr) was washed twice with 90 ml deionized water and further purified 5 times using an 80% aqueous solution of ethanol, till the decanted solvent following centrifugation became completely colorless. The green solid was then immersed in 30 mM aqueous NH_4F solution and stirred at 60 °C for 10 h (1 g:150 ml). The suspension was centrifuged, after which the solid was washed 5 times with deionized water at 60 °C. The green solid was then washed three times with 70 ml DMF, and 5 times with 75 ml deionized water, and finally dried in air at 75 °C for 2 days and 95 °C for 2 days.

The first step involved in the synthesis of MWCNT/MIL-101(Cr)