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Manufacturing of metal-organic framework monoliths and their application in CO_2 adsorption

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ABSTRACT

An important class of novel mesoporous and microporous adsorbents like metal-organic frameworks (MOFs) are normally produced in powder form. This paper presents a generic method of manufacturing and characterisation of these materials into low pressure drop and energy saving monolithic structures for industrial applications. One of the MOF candidates that was considered in this study was MIL-101 (Cr) ($[Cr_3O(OH)(H_2O)_2(bdc)_3].xH_2O$; bdc = 1,4-benzenedicarboxylate), and the model contaminant gas tested was carbon dioxide (CO_2). MIL-101 (Cr) monoliths were manufactured by paste extrusion techniques from the synthesized MIL-101 (Cr) powder. These MIL-101 (Cr) monoliths were then characterised using powder X-ray diffraction (PXRD), scanning electron microscopy (SEM), mercury intrusion porosimetry (MIP), radial compression tests and intelligent gravimetric analysis (IGA). Adsorption properties of the prepared MIL-101 (Cr) powder and monoliths were determined from their pure CO_2 sorption isotherms and dynamic adsorption breakthrough curves, that were carried out using high concentration (40% v/v) CO_2 challenge. Results have demonstrated that the resulting MIL-101 (Cr) monoliths were highly porous, mechanically strong on compressive loading, thermally regenerable with comparable CO_2 adsorption capacity to the synthesized MIL-101 (Cr) powder. From breakthrough curves, mass transfer characteristics such as mass transfer zone velocity and length of the prepared MIL-101 (Cr) monoliths have also been evaluated in this study.

1. Introduction

New porous materials such as metal-organic frameworks (MOFs) have attracted a great deal of research interest, particularly in gas adsorption applications due to their large pore size [1], high porosity [2], large surface area [1–4], thermal and chemical stabilities [1,4], adsorption capacity [1,5,6] and low density [3]. Their three-dimensional crystalline structures are built from metal ions or metallic clusters and organic linkers. A conventional method for synthesizing MOFs is by solvothermal reaction, which normally produced fine-particle powders [7]. For these MOFs powders to be applicable industrially, they need to be converted into a structure, which could be in the form of monoliths, beads, pellets, foams, etc. The most economical and energy efficient structure for use in any adsorption systems could be in the form of monoliths because its structure has low pressure drop and high mass transfer rates compared to other structures [8–11]. Experimental studies on MOFs for adsorption processes are mostly performed using its powder form and the generation of structured MOFs, particularly monolithic structure for industrial adsorption processes is rare. The fabrication of MOFs monoliths was first reported by Küsgens et al. [12] and they found that the *in situ* synthesis of a well-known MOF, i.e. copper(II) benzene-1,3,5-tricarboxylate [$Cu_3(BTC)_2$] on cordierite monoliths has low achievable adsorption capacity than manufacturing pure MOF monoliths. Although it is possible to manufacture pure $Cu_3(BTC)_2$ monoliths, their application for carbon dioxide (CO_2) adsorption in humid conditions is not sustainable because $Cu_3(BTC)_2$ has a poor hydrothermal stability, as proven by Liu et al. [13].

The manufacturing of MOF monoliths from its powder form and their use in gas adsorption processes, particularly for biogas upgrading application, will be presented in this paper. The contaminant/adsorbate gas to be studied in this paper was CO_2 of high concentration, i.e. 40% (v/v); the typical CO_2 content found in biogas. One of the MOFs that was selected as a model adsorbent

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material for this study was MIL-101 (Cr) ($[Cr_3O(OH)(-H_2O)_2(bdc)_3].xH_2O$; bdc = 1,4-benzenedicarboxylate). MIL-101 (Cr) was chosen because it is a stable adsorbent material under ambient atmosphere (for months) and even in the presence of various organic solvents and/or water [1]. Several studies [1,14,15] have demonstrated that MIL-101 (Cr) has a high adsorption capacity for CO_2; from 22.90 mmol g^{-1} at 25 °C and 30 bar [16] up to 40 mmol g^{-1} at 25 °C and 500 bar [17]. Other properties of MIL-101 (Cr) that need to be considered when developing a structured adsorbent for industrial applications with efficient adsorption performance are their pore properties and thermal stability. MIL-101 (Cr) has large pore sizes, ranging from 2.90 nm to 3.40 nm [1], large Langmuir surface area (using nitrogen isotherms) of 5900 ± 300 m^2 g^{-1} [1] and thermally stable up to 275 °C [1,15].

The process of manufacturing MIL-101 (Cr) monoliths by paste extrusion techniques will be described in this paper. Physical (crystal structure, surface morphology, pore structure and mechanical strength) and adsorptive properties (CO_2 sorption isotherms and adsorption breakthrough curves) of these MIL-101 (Cr) monoliths will then be characterized using powder X-ray diffraction (PXRD), scanning electron microscopy (SEM), mercury intrusion porosimetry (MIP), radial compression strength testing, intelligent gravimetric analysis (IGA) and dynamic adsorption flow breakthrough experiments. The aim of this paper is to show that MIL-101 (Cr) powder can be made into monolithic structure that is porous, mechanically strong on radial compression loading, thermally stable after adsorption–regeneration cycles and could be used as a low pressure drop sorption device for adsorbing high concentration of CO_2 from gas streams.

2. Experimental

2.1. Materials

Chromium(III) nitrate nonahydrate (99%) and 1,4-benzenedicarboxylic acid (commonly known as terephthalic acid) (≥99%) were purchased from Acros Organics (UK), ethanol (≥99.8%) was purchased from Sigma–Aldrich Co. (USA), bentonite clay was purchased from Bath Potters' Supplies Ltd. (UK) and mercury was purchased from Fisher Scientific (UK). The adsorbate gas for adsorption experiments was CO_2 with a concentration of 40% (v/v) in air and it was purchased from BOC Ltd. (UK). All chemicals and gas were used as obtained from commercial sources, without further purification.

2.2. Synthesis of MIL-101 (Cr) powder

MIL-101 (Cr) powder was prepared by the modification of the synthesis described by Bromberg et al. [18], which eliminates the use of the toxic and highly corrosive hydrofluoric acid in the reaction. A mixture of chromium(III) nitrate (1.05 g), 1.4-benzendicarboxylic acid (0.40 g) and distilled water (12.25 g) was placed in an autoclave and heated to 220 °C for 8 h. The autoclave was then cooled to room temperature. Insoluble green crystals of MIL-101 (Cr) were collected by centrifugation, washing with distilled water and dried at room temperature. As-synthesized MIL-101 (Cr) powder was then obtained.

2.3. Purification of MIL-101 (Cr) powder

The prepared as-synthesized MIL-101 (Cr) powder was treated with ethanol at 80 °C for 4 h. Purified green crystals of MIL-101 (Cr) were then collected by centrifugation, washing with ethanol and dried at room temperature. The resulting product obtained was purified MIL-101 (Cr) powder.

2.4. Preparation of MIL-101 (Cr) monoliths

MIL-101 (Cr) monoliths were prepared by paste extrusion techniques from its as-synthesized and purified powders. The binding agent that was used in this work was bentonite clay. Green MIL-101 (Cr) powder, bentonite clay and water were mixed together to form a paste and allowed to mature at room temperature. When the MOF paste has matured into a workable paste, it was extruded into monoliths on a single screw extruder. Extruded MOF monoliths were dried in a temperature controlled chamber at 10 °C for several days before they were fired in a kiln at 150 °C for about 33 h to form a strong and solid monolithic structure. Fired MIL-101 (Cr) monoliths were cut into 7.00 cm lengths for the dynamic adsorption breakthrough study. MIL-101 (Cr) monoliths containing 60% (w/w) of as-synthesized MIL-101 (Cr), 60% (w/w) and 75% (w/w) of purified MIL-101 (Cr) were prepared. All MIL-101 (Cr) monoliths that were prepared using this procedure have square channels with equal wall thickness, t_w, and channel size, d_c, of 0.90 mm.

2.5. Characterisation of MIL-101 (Cr) powder and monoliths

Powder and monolith samples of the as-synthesized and purified MIL-101 (Cr) were analysed by PXRD on a Bruker AXS D8 Advance diffractometer with copper radiation in 2θ angles ranging from 3° to 40°. Surface morphologies of the as-synthesized and purified MIL-101 (Cr) powder and monolith was examined by SEM using a JEOL JSM-6480 LV microscope, in which the samples were coated with a thin layer of gold using Edwards S150B sputter coater. Pore structures of the as-synthesized and purified MIL-101 (Cr) powder and monoliths were characterized by MIP on Micromeritics AutoPore III, where mercury was forced into the pores of the test samples at elevated pressures. Mechanical radial compression strengths of the 60% (w/w) and 75% (w/w) purified MIL-101 (Cr) monoliths were determined by performing radial compression tests on the Instron 3369 Universal Tester machine with a compression rate of 0.50 mm min^{-1}.

2.6. Adsorption properties of MIL-101 (Cr) powder and monoliths

Pure CO_2 sorption properties of purified MIL-101 (Cr) powder and monolith (containing 60% (w/w) MIL-101 (Cr) and 40% (w/w) binder) were evaluated using its sorption isotherms for pressure ranging from 0 bar to 4.50 bar at 20 °C and 25 °C on the Hiden intelligent gravimetric analyser. Meanwhile, the dynamic adsorption of CO_2 on MIL-101 (Cr) monoliths was investigated on an adsorption flow-breakthrough apparatus. The apparatus consists of a feed gas flow system, an adsorption column and an effluent gas analytical system, as illustrated in Fig. 1. Prior to the start of the adsorption experiments, all test samples were regenerated at 150 °C for at least 12 h.

Regenerated MIL-101 (Cr) monoliths with a length of 7.00 cm and a diameter of 21.47 mm was packed tightly and held in the centre of the steel tubular adsorption column by wrapping the inlet end of the monolith with PTFE gas sealant tape and a nitrile O-ring so that the feed gas only flows through the monolith channels and not around the monolith wall. A flow distributor was placed on the inlet end of the adsorption column to ensure uniform gas flow through the monolith channels. The packed adsorption column was mounted vertically on the adsorption flow-breakthrough apparatus. In this study, CO_2 gas with a concentration of 40% (v/v) was used as the feed adsorbate gas and compressed air was used as the purging gas for cleaning the lines of the adsorption system. All adsorption experiments were performed with a feed gas flow rate