3D-printed SAPO-34 monoliths for gas separation

Sarah Couck [a], Julien Cousin-Saint-Remi [a], Stijn Van der Perre [a], Gino V. Baron [a], Clara Minas [b], Patrick Ruch [c], Joeri F.M. Denayer [a, *]

[a] *Chemical Engineering Department, Vrije Universiteit Brussel, Pleinlaan 2, 1050 Brussel, Belgium*
[b] *Complex Materials, Department of Materials, ETH Zürich, Vladimir-Prelog-Weg 5, 8093 Zürich, Switzerland*
[c] *IBM Research – Zurich, Säumerstrasse 4, 8803 Rüschlikon, Switzerland*

ARTICLE INFO

ABSTRACT

A 3D printing method (the Direct Ink writing, DIW, method) is applied to produce SAPO-34 zeolite based structured adsorbents with the shape of a honeycomb-like monolith. The use of the 3D printing technique gives this structure a well-defined and easily adaptable geometry. As binder material, methyl cellulose was used. The SAPO-34 monolith was characterized by SEM as well as Ar and Hg porosimetry. The CO_2 adsorption affinity, capacity and heat of adsorption were determined by recording high pressure adsorption isotherms at different temperatures, using the gravimetric technique. The separation potential was investigated by means of breakthrough experiments with mixtures of CO_2 and N_2. The experimental selectivity of CO_2/N_2 separation was compared to the selectivity as predicted by the Ideal Adsorbed Solution Theory. A drop in capacity was noticed during the experiments and N_2 capacities were close to zero or slightly negative due to the very low adsorption, meaning absolute selectivity values could not be determined. However, due to the low N_2 capacity, experimental selectivity is estimated to be excellent as was predicted with IAST. While the 3D printing is found to be a practical, fast and flexible route to generate monolithic adsorbent structures, improvements in formulation are required in terms of sample robustness for handling purposes and heat transfer characteristics of the obtained monoliths during gas separation.

© 2017 Elsevier Inc. All rights reserved.

1. Introduction

In the past decade, it was demonstrated that structuring adsorbents into monolithic structures has some major advantages as compared to traditional shaped adsorbents like beads, granules or pellets. Monolithic structures lead to improvements in for example, pressure drop, mass transfer and/or heat transfer [1–6]. Such monolithic structures were mostly tested for CO_2 separation applications [7–13]. To prepare these monolithic structures, two main routes exist, e.g. direct extrusion of the adsorbent or attaching an adsorbent layer to a support monolith (for instance by means of wash-coating, dip-coating, or crystal growth). Apart from a limited flexibility, these methods of preparation do have some disadvantages. When using a support monolith with an adsorbent coating, a large part of the monolithic body does not contribute to the adsorption process and thus provides a poor volumetric yield of the adsorbent bed. Extruded monoliths on the other hand are prepared from the active material itself, but the shape of the resulting monolith is determined by the extrusion die, which has limited variability. Together with the high cost of the extrusion die, this restricts the possibilities to study the effect of structural properties (e.g. effect of wall thickness and channel width on mass and heat transfer) in a systematic way.

The emerging technique of 3D printing can offer a solution to the limitations of extrusion as it has a much higher level in freedom of operation. Therefore, it provides an excellent research tool, allowing to generate a wide variety in structures suitable for lab scale adsorption studies. 3D printing, also known as additive manufacturing, comprises several printing methods like fused deposition modelling (FDM), direct ink writing (DIW), stereolithography (SLA), selective laser sintering (SLS) and many more designations [14,15]. Although the first working 3D printer was already patented in 1984 (based on the SLA principle) [16], it is only recently that 3D printing has become a very popular commercial technique.

Also in adsorption, catalysis or separation processes, this 3D printing technique is becoming a popular tool. In the field of heterogeneous catalysis, 3D printing has been applied to prepare a variety of structured catalysts as an alternative to honeycomb structures. Tubio et al. reported the 3D printing of a Cu/Al$_2$O$_3$ monolithic catalyst with excellent performance in the Ullmann reaction [17]. Michorczyk et al. described the generation of an Al based catalyst, by first printing the template very precisely with 3D printing, then filling the template with the catalyst and as a last step burning away the template, leaving a well-defined catalytic reactor [18]. Azuaje et al. reported the direct printing of an Al catalyst that acts as a Lewis acid in the Biginelli and Hantzsch reactions [19]. Fee et al. even printed an entire chromatographic column, with the internal column packing, flow connectors and distributors present in the 3D printed column itself [20]. Recent advances by Minas et al. have enabled the printing of highly porous ceramics using emulsions and foams as precursor inks, offering the opportunity to tune the thermal and mechanical properties of such structures by modifying the porosity of the printed struts themselves [21].

At this moment, only a few publications dealing with 3D-printed structures in the field of adsorption are available. Thakkar et al. recently studied CO$_2$ capture by adsorption on 3D-printed zeolite monoliths (5A and 13X) and aminosilica adsorbent structures [22,23]. These 3D-printed adsorbents were based on the deposition of a paste in a layer-by-layer fashion, leading to a well-defined monolith in terms of wall thickness and channel width. The authors concluded that these 3D-printed monoliths are very promising for CO$_2$ capture and thus offer an alternative approach for structuring adsorbents.

In our previous work [24], a 3D-printed monolith of zeolite ZSM-5 was generated by three-dimensional fibre deposition (3DFD) using a 3D-printing method developed by VITO (Vlaams Instituut voor Technologische Ontwikkeling, Belgium) [25,26]. A paste, obtained by mixing the zeolite powder with bentonite, silica and water was printed into an open structure with stacked fibres of 400 μm diameter. This structured adsorbent showed excellent performance in the separation of CO$_2$ from N$_2$ or CH$_4$.

One critical aspect in the development in structured adsorbents is the preparation of the paste that is used in the extrusion or 3D-printing process. It should allow to deposit the structure in a smooth way, but also result in a robust structure that retains a large adsorption capacity. For inorganic porous solids, very often clay or silica based binders or used. Such binder materials require a high temperature treatment to obtain a strong and solid structure. Alternatively, polymeric binders allow to obtain rigid structures without the need for a high temperature treatment. This is interesting when the porous material itself does not withstand such a high temperature treatment.

In this work, we report on the synthesis of a 3D-printed monolith comprising SAPO-34 zeolite, using a polymeric binder material (Methyl cellulose). The monolith is made by printing the zeolite fibres in a layer-upon-layer fashion in a well-defined way. The resulting monolith was tested for adsorption and separation of CO$_2$ and N$_2$ by means of isotherms and breakthrough experiments.

2. Materials and methods

2.1. Sample preparation

SAPO-34 zeolite (product name: AQSOA Z02) was purchased from Mitsubishi Chemical and used to prepare a paste for 3D-printing. 50 wt% SAPO-34 suspensions were prepared by the addition of the zeolite powder to a 0.6 wt% Polyacrylic acid (Poly(acrylic acid sodium salt), Sigma-Aldrich Chemie GmbH,

Germany) solution. In a second type of formulation, 5 wt% graphite (in respect to the SAPO-34 powder) was added to this mixture. Gelation was induced through the incorporation of 2–3 wt% Methylcellulose (Methocel, DOW, Germany) for both formulations.

Cylinders with a diameter of 1 cm and a grid like filling were printed with a speed of 4 mm/s using a pressure-controlled direct ink wiring system (3D Discovery, RegenHu Ltd., Switzerland). A nozzle diameter of 330 μm was used, while the off-set in z-direction was set to 150 μm. Samples were dried at ambient conditions for 48 h.

2.2. Characterization and isotherms

The topology of the monoliths, including the size of the channels, the surface of the fibers and agglomeration of the crystals, was analyzed by scanning electron microscopy (JEOL). Ar porosimetry at 87 K was performed with an Autosorb AS-1 from Quantachrome. BET surface area was calculated and pore volume was estimated with the Gurvich rule (p/p$_0$ = 0.2). Low pressure (0–1 bar) CO$_2$ isotherms were determined at different temperatures (273 K–303 K–323 K) with an Autosorb device. Prior to these experiments, the samples were outgassed at a pressure of 0.01 Pa and a temperature of 100 °C overnight, after pre-activation in a vacuum oven. From these isotherm measurements, isosteric heats of adsorption were calculated using the Clausius-Clapeyron equation. The monolithic structures were further characterized with Hg porosimetry (Thermo-Finnigan porosimeter 2000), with a measurement starting at 1 bar and going up to a pressure of 2000 bar. The thermal behaviour was investigated using thermogravimetric (TG) and differential scanning calorimetry (DSC) analysis (SENSYS Evo TG/DSC; SETARAM Instrumentation, France) to determine the heat of adsorption for CO$_2$ on different SAPO-34 samples. An aluminium crucible, filled with SAPO-34 or SAPO-34/graphite monolith sample, was activated at 373 K under an He flow for several hours, and then subjected to a CO$_2$ stream (P = 1 bar). High pressure single component isotherms of CO$_2$, CH$_4$ and N$_2$ at 303 K were measured with an automatic gas dosing system and magnetic suspension balance from Rubotherm GmbH. Prior to these measurements, the materials were activated at 373 K under vacuum.

2.3. Separation experiments

The separation potential of the monoliths was assessed by performing breakthrough experiments. A detailed description of the setup used for these experiments can be found in earlier work [27]. The amounts adsorbed resulting from the breakthrough times were calculated using the method of Peter et al. [28]. As the monolithic structures were printed with a diameter of 1 cm, they fitted into a 1/2″ stainless steel column. To obtain a reasonable length, different monolith structures were stacked on top of each other to form a length of 5 cm. The different monolith segments were wrapped with Teflon tape in order to avoid gas escaping around the structure. Some monolith segments were also crushed and sieved to obtain 450–600 μm diameter pellets. These pellets were then transferred to a 1/8″ stainless steel column. Breakthrough experiments were conducted with a total flow rate of 40 Nml/min with pure N$_2$ or CO$_2$ or a mixture of those gases. Before each breakthrough experiment, the material was subjected to a temperature increase to 373 K under an inert He flow.

The experimentally obtained selectivity was compared to the selectivity predicated by the Ideal Adsorbed Solution Theory, using the Langmuir fit of the experimental high pressure pure component adsorption isotherm as input to the model [29].