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Clay honeycomb monoliths as low cost CO_2 adsorbents

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ABSTRACT

Clay honeycomb monoliths were manufactured from a natural montmorillonite and used for CO_2 adsorption, their performance being compared with that of the same clay but in the form of powder. Volumetric adsorption isotherms, thermogravimetric studies, temperature-programmed desorption experiments and transient kinetic analysis, the two latter followed by mass spectrometry, were employed to investigate the interaction of the samples with CO_2, both under static and dynamic conditions, and at different temperatures. This research demonstrated that the honeycomb monoliths kept the adsorptive properties of the starting material in terms of capture capacity (around 15 mg/g), Henry constant, heat of adsorption and activation energy. Most of retained CO_2 was weakly adsorbed, the temperature needed for its release being 130 °C, an appropriate value which is sufficiently high to avoid undesirable desorption while being low enough to minimize the costs derived from controlled regeneration for further CO_2 reuse. The kinetics of the CO_2 uptake over the monolith (though of second order like over the powder) was slightly different, allowing a wider operative window for a highly efficient CO_2 removal. These results suggest the potential of the honeycomb monolithic design for an even more competitive use of clays as low cost CO_2 filters.

1. Introduction

Nowadays it is increasingly attractive the combination of capture and utilization of CO_2 as a means to address the storage limitations of Carbon Capture and Sequestration (CCS) technology and enhance sustainability for the benefit of future generations [1]. Nevertheless, there is still room for improvement in the different steps of such integrated approach. For example, in the particular context of CO_2 sequestration, clay materials have many advantages in comparison with the most commonly used adsorbents such as those based on solid amines [2], carbons [2,3], graphite/graphene [4], zeolites [2], metal-organic frameworks [2,5], mesoporous silica [6,7], alkaline earth oxides such as MgO [8], CaO [9,10] or BaO [11], transition metal oxides such as CuO [12] and ZnO [13], rare earth oxides such as CeO_2 [14], and many others (polymers, alkali metal carbonates, immobilized ionic liquids, boron nitrides, alkali zirconates or silicates [8]). Clay materials have high surface area, and both high mechanical and chemical stability. In addition, they have low cost and relative easiness in availability, regeneration and production in large enough quantities [8].

In spite of the fact that the use of clays for CO_2 capture has also attracted some attention recently, their use in the form of honeycomb monoliths for this application, compared to other uses related to environmental protection, is still surprisingly missing [15]. Nevertheless, if high volumes of gaseous effluents containing relatively low CO_2 concentration had to be treated, such design would be better to ensure low pressure drop [16]. Furthermore, honeycomb monolithic filters, being unitary structures, would facilitate both handling and replacement upon saturation. In this sense, many natural clays have ideal plastic properties to obtain pastes that can be extruded as honeycombs even without needing the use of additives [17]. In fact, in previous studies we easily extruded honeycomb-shaped monoliths using natural clays for different environmental applications such as VOCs adsorption [18,19], methylene blue removal from aqueous streams [20] or biofuel combustion [21].

The above claimed lack in the state-of-art of CO_2 adsorption is even more astonishing taking into account that, instead of developing materials, new researches have used low cost materials into a structural framework to improve adsorption capacity, such as metal-organic framework, nanoporous materials and foam-like materials [22]. However, to our knowledge, no similar work can be found regarding the use of honeycomb monoliths for CO_2 sequestration. Consequently, this paper intends to fill this gap by manufacturing clay honeycomb monoliths and further applying them to remove CO_2 from a gaseous flow. Attention is paid not only to the amount of CO_2 that can be adsorbed but also to the

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strength of such interaction which can be critical either to avoid undesired pollutant return to the environment or for the controlled regeneration of the adsorbent in case of need. The kinetics of the process is investigated as well. Moreover, although at lab scale conditions, a general comparison with the performance of the clay in the form of powder is made in order to better evaluate the potential of these filters prototypes for a further application under more realistic conditions.

2. Material and methods

2.1. Samples preparation

The natural clay studied in this work was provided by Süd-Chemie España S.L. with the name of Esquivias and came from deposits located at the centre of Spain (Toledo), its market cost being approx. 10 €/Ton (according to supplier information). It was selected among other natural clays after exhibiting in a previous study the best performance for CO_2 adsorption in the form of powder as originally received [23]. Fig. 1 summarizes the main characteristics of this clay which derived from its previous characterization. It should be highlighted its partially mesoporous character (rendering relatively high specific surface area, above 200 m^2/g) (1.a), high thermal stability (up to 600 °C) (1.b), and appropriate granulometry (mean size around 10 μm) and rheological properties (liquid limit = 50% and plasticity index = 26%) (1.c) for extrusion even without additives [24]. Regarding its structure (1.d and 1.e) and composition (1.f) both were consistent with the nature of a kerolitic montmorillonite, anticipated by the supplier. In particular, the main phase detected by XRD was a $CaMg_2AlSi_4(OH)_2{\cdot}H_2O$ montmorillonite (PDF file 02-0239) with the presence of quartz.

The clay honeycomb monoliths were obtained by extrusion of a paste, previously prepared by mixing the above fine starting powder with the adequate amount of water (0.42 ml/g of paste). The resulting green monoliths were dried overnight at 60 °C and subsequently calcined at 300 °C for 5 h. This treatment was chosen from the thermogravimetric analysis results as the one allowing optimal enhancement of the mechanical resistance while preserving the clay structure, as learned from the previous experience with other clays [20]. The final monoliths presented a honeycomb-type circular section with a diameter of 1.4 cm, a density of approx. 50 cells/cm^2, 0.33 mm of wall thickness and a 72% open frontal area (Fig. 2). Their textural properties were measured by N_2 physisorption at −196 °C over pre-evacuated at 150 °C for 1 h small monolithic pieces (4 × 4 channels) employing a Quantachrome Autosorb iQ automatic device. The results were similar to those of the powdered clay (compare the corresponding isotherms—both type II with H4 hysteresis loop—as well as BET surface area and pore volume included in Figs. 1 and 2).

2.2. Study of the interaction with CO_2

CO_2 volumetric adsorption experiments were carried out in an automatic Micromeritics ASAP 2020C instrument, using both clay monolith pieces (5 × 5 channels) and clay powder. Isotherms were obtained at five different temperatures: 35, 100, 200, 300 and 500 °C. Before the analysis the sample was submitted to a treatment consisting of a cleaning in a flow of He (60 ml/min) at 150 °C for 1 h, with a heating rate of 10 °C/min. To estimate the irreversible adsorption component, a second isotherm after previous evacuation at the selected adsorption temperature was also recorded and subtracted from the first one in each case.

The interaction of the samples with CO_2 was also studied under dynamic conditions using both thermogravimetry and mass spectrometry (MS) for the analysis, aimed to quantify the amount of CO_2 retained through the weight gain after exposure to a CO_2 flow, and to evaluate the strength of the interaction by further Temperature-Programmed Desorption (TPD) experiments, respectively. In the first case, the study was carried out in a SDT Q600 thermobalance over both powder and small pieces of the monolith walls. Prior to the analysis, the sample was submitted to the same cleaning pre-treatment than the one applied before running the volumetric adsorption experiments. Subsequently, it was subjected to a 100 ml/min flow of CO_2(40%)/He for 1 h. This was performed operating at different temperatures: 35, 50, 75, 100, 200, 300 and 500 °C. In the case of TPD, the sample was pre-cleaned as before and further submitted to pure CO_2 (5 ml/min) for 1 h. Then the flow switched to He (60 ml/min) heating up to 900 °C with a 10°C/min rate. This time the analysis was performed over entire 1.1 cm long monoliths as well as over the reference clay powder. Same sample amount (1.3 g) was used in both cases for comparative purposes. To study the reuse potential of the clay honeycomb monoliths we also carried out, over the same piece of honeycomb sample, consecutive cycles of adsorption of pure CO_2 (5 ml/min) at 35 °C for 1 h and desorption in He flow (60 ml/min) from 35 to 350 °C, keeping this temperature for 1 h.

Finally, kinetic transient experiments followed also by mass spectrometry were carried out, by monitoring the response to a switch of the flow from Ar to CO_2(17%)/He over as above pre-cleaned samples. The sample load (1.3 g), the reactor dimensions and the flow were properly adjusted to ensure same contact time (3 s) for the experiments run over the monoliths (entire section, 1.1 cm long) and the powder. In the case of the monoliths, small pieces of quartz were located at the reactor inlet to allow a turbulent flow. Blank experiments were also performed to consider the instrumental contribution to the response during the transient experiments.

3. Results and discussion

3.1. Volumetric adsorption of CO_2

Fig. 3 shows the isotherms recorded during the volumetric CO_2 adsorption experiments performed over both the clay powder and clay honeycomb monoliths at different temperatures. Although not represented the second isotherm obtained after evacuation was very similar to the first one in each case. Table 1 summarizes the main results derived from processing these CO_2 isotherms. As expected, for both samples the quantity of CO_2 adsorbed decreases with temperature. Also remarkable, most of the adsorption is reversible. At 35 °C and 1 atm the performance of the powder is slightly better than that of the monolith (0.38 mmol CO_2/g *versus* 0.34 mmol CO_2/g). Nevertheless, for the rest of temperatures studied, their behaviour is almost equal. It is fair to say that the adsorption capacity of the monolith at 35 °C, equivalent to 15 mg CO_2/g, is certainly lower than that reported for other low cost adsorbents at 25-45 °C [22], including montmorillonite- [25] or other bentonites-based [26] materials; however, most of these references were prepared from more or less sophisticated pre-treatments of the starting materials such as acid activation or surface modification by functional groups to improve the adsorption capacity, while the clay here investigated did not require any additive (nor even for its extrusion) so reducing its preparative costs.

From the above data and following the procedure reported in literature in similar studies with other adsorbents [5], it has been possible to estimate also the Henry constant (K) for three adsorption temperatures (T), taken as representative of the whole range investigated (Table 2).

To calculate the Henry constant, all isotherms have been correlated with the model of Langmuir

$$\theta = a_m \frac{\alpha \cdot p}{1 + \alpha \cdot p} \quad (1)$$

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