Available online at www.sciencedirect.com
SCIENCE DIRECT
C. R. Chimie 9 (2006) 1215–1220
COMPTES RENDUS CHIMIE
http://france.elsevier.com/direct/CRAS2C/

Preliminary communication / Communication

Originally prepared carbon-based honeycomb monoliths with potential application as VOCs adsorbents

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Received 29 September 2005; accepted after revision 2 February 2006
Available online 10 March 2006

Abstract

Integral 90 wt% carbon-honeycomb lab-scale monoliths prepared from coal are characterized and applied to adsorb *o*-xylene. Textural characterization shows that the monoliths obtained after activation of the carbon exhibit appropriate porosity for their use as adsorbents. Their total capacity to retain *o*-xylene proves to be similar to that previously reported for studies under dynamic conditions on activated carbons but in the form of powder. ***To cite this article: J.M. Gatica et al., C. R. Chimie 9 (2006)***.

Résumé

Des monolithes à base de 90 % en poids de carbone en forme de nid d'abeille, préparés à l'échelle du laboratoire, ont fait l'objet d'études de caractérisation physicochimique et d'évaluation de leur capacité d'adsorption vis-à-vis de l'*o*-xylène. Les résultats de la caractérisation texturale ont montré que les monolithes obtenus après activation possèdent une porosité permettant leur utilisation comme adsorbants. Les tests d'adsorption ont montré que ces monolithes possèdent une capacité d'adsorption simillaire à celle trouvée dans la littérature pour les solides sous forme de poudre à base de carbone activé étudiés en conditions dynamiques. ***Pour citer cet article : J.M. Gatica et al., C. R. Chimie 9 (2006)***.

Keywords: Carbon monoliths; Dynamical adsorption; Breakthrough curves; FTIR analysis; *o*-Xylene

Mots clés : Monolithes de carbone ; Adsorption dynamique ; Courbes de percée ; Analyses IRTF ; *o*-Xylène

1. Introduction

Nowadays, emission to air of volatile organic compounds (VOCs), compounds with vapor pressures greater than 133.3 Pa (1 mmHg) at room temperature, is considered one of the most concerning forms of atmospheric pollution due to their multiple harmful effects (viz. toxic character, formation of ozone) [1a]. They can be released from industrial processes using solvents, polymers and resins such as those involved in painting and coating operations. Along with catalysis, adsorption is an established abatement technology,

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1631-0748/$ - see front matter
doi:10.1016/j.crci.2006.02.002

activated carbons being one of the best candidates for such application [2]. Usually, carbon-based adsorbents are rather employed as beds of powdered or granulated materials than in the monolithic form as the rheological properties of carbon make it a complicated material for processing through extrusion. Nonetheless, compared with the conventional packed beds, monolithic structures offer well-known advantages for processes where pressure drop has a significant economic impact. In addition, monoliths represent an easier handling design [1b].

To the best of our knowledge, the studies of honeycomb monoliths of activated carbons found in literature correspond to the use of carbon as deposited on a ceramic monolith [3,4], and thus not introduced before extrusion, or if extruded, either there is no indication of how extrudability of the carbonaceous paste is finally achieved or carbon used is not the major component or derives from a polymeric resin instead of consisting of natural coal [5–7]. Other strategy is the use of cellulose with the desired structure which is subjected to impregnation with pitch as carbon precursor [8]. There is no doubt that the topic still attracts, as new and refined methods are reported. In this regard, recently a carbon monolith (although not in the honeycomb form) was synthesized as a replica of a tailored-pore silica monolith by using a complex and time-consuming method based on templating procedure and sol-gel process [9].

In this sense, we have recently extended preparation methods based on the techniques that are usually employed with ceramic materials to carbonaceous pastes, what has allowed us to obtain, among other compositions, integral 90 wt% carbon-honeycomb lab-scale monoliths starting from coal [10]. This original experimental approach only implies, in contrast to other methods, the measurement of plastic properties just related with the humidity of the paste to be extruded [11]. The monoliths hereby obtained can be further modified by subsequent activation. Mechanical and textural properties of the resulting monoliths have been studied here, the latter being correlated with their adsorptive performance which is illustrated through an application to adsorption of a model VOC pollutant such as *o*-xylene.

2. Experimental

2.1. Materials

The honeycomb square section monoliths (with 4 cells cm^{-2}, in a 2×2 configuration) tested in the present work were prepared from natural coal provided by the National Institute of Carbon in Spain, whose composition was 30 wt% of volatile and less than 6 wt% of ashes, and 75 vol% of vitrinite phase concerning its maceral composition. Elemental analysis of the coal gave the following results: C (72.7 wt%), H (1.8 wt %), N (0.3 wt%) and S (0.1 wt%). As it presented initially a high average particle size (3 mm), it was crushed and sieved until its conversion into grains finer than 250 μm.

2.2. Carbon-based monoliths preparation

The honeycomb monoliths here prepared were obtained by means of extrusion of a carbon-based material. To obtain a dough with adequate rheological properties for the extrusion, some additives were used besides water: 9.5% silicate clay (ARGI-2000 from VICAR, S. A.), 2.5% glycerine, 1.9% methylcellulose and 0.3% aluminum phosphate dissolved in *o*-phosphoric acid (weight percentages referred to the extrudable paste excluding water). Measurement of the liquid limit (LL) and plasticity index (PI) of different samples allowed, in a previous stage, to optimize the composition of the paste until it fulfilled simultaneously the extrudability prerequisites, $40\% < LL < 60\%$ and $10\% < PI < 30\%$. Thus, $LL = 47\%$ and $PI = 24\%$ were obtained for the above described paste. After its final extrusion, the green monoliths were dried in an oven at 80 °C overnight, and then underwent a thermal treatment consisting, first, of a preoxidation (air, 250 °C, 24 h) in order to prevent a pseudoplastic state by oxygenated cross-links, which allows further activation and pore development [12]. Subsequently, carbonization (Ar, 840 °C, 1 h) and activation (H_2O, 250 Torr/Ar, 860 °C, up to a burn-off degree of 15 wt%) treatments were carried out to eliminate the additives and to develop the porous structure required for application of the monoliths as adsorbents. Further details of the experimental methodology to obtain coal-based honeycomb monoliths have been previously reported [10]. Fig. 1 shows an image of a typical monolith obtained by the above described procedure.

2.3. Characterization techniques

Textural characterization of both the starting material and the final activated monoliths has been carried out by measuring true and apparent densities (mercury at 0.1 MPa), mercury porosimetry and physical adsorption of N_2 at −196 °C (Table 1). For this study, a Micromeritics 1320 Autopycnometer, a Macropores Unit 120