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Ceramic papers containing Y zeolite for toluene removal

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ABSTRACT

A papermaking technique with a dual polyelectrolyte retention system was used for the preparation of NaY zeolite-containing papers, which implied the use of cationic and anionic polymers. Two kinds of fibers were employed, either cellulosic or ceramic ones, and accordingly papers with different characteristics were obtained: those that only contained cellulosic fibers for low temperature applications, cellulosic papers, and those prepared using both cellulosic and ceramic fibers – ceramic papers – for high temperature applications. Although a decrease in their mechanical properties due to calcination was observed, zeolitic ceramic papers resulted easy to handle for practical applications.

Zeolite was quantified through BET surface area measurements. SEM images indicated a good dispersion of zeolite particles within the cellulosic paper whereas in the ceramic paper they appeared anchored on ceramic fibers.

The zeolitic papers prepared resulted efficient as toluene sorbents, the adsorption capacities of zeolitic ceramic papers being higher than those of zeolitic cellulosic papers. In the case of zeolitic cellulosic papers, the amounts of released toluene were lower than those of adsorbed toluene, implying that the treatment up to 160 °C did not completely eliminate the hydrocarbon. Also, TPD profiles showed that toluene is chemically retained up to high temperatures (ca. 420 °C) in zeolitic ceramic papers.

Toluene adsorption values demonstrate that zeolite dispersed into the cellulose/ceramic matrix is as effective as powder massive zeolite in retaining the hydrocarbon, which highlights the potential application of these zeolitic structures as sorbent materials both for low and high temperatures.

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1. Introduction

Volatile organic compounds (VOCs) vaporize easily at low temperatures and include most thinners, solvents, degreasers, cleaners, lubricants and liquid fuels. The most common VOCs include acetaldehyde, acetone, benzene, ethyl acetate, carbon tetrachloride, ethylene glycol, formaldehyde, heptane, hexane, isopropyl alcohol, methyl ethyl ketone, methyl chloride, monomethyl ether, naphthalene, toluene and xylene. VOCs pollutants can come from indoor and outdoor sources. Indoor VOCs pollution often originates from household products such as office supplies, insulating materials, cleaning products, and pressed woods, or may originate from tobacco smoke [1]. On the other hand, outdoor VOCs pollution is mainly originated from emissions of industrial processes and automobile exhausts. From the environmental point of view, it is necessary to limit and control vapor emissions, which affect climate change, the growth and decay of plants, and the health of humans and animals [2,3].

Toluene is a typical indoor pollutant and its discharge may produce irritation of the eyes and the respiratory tract, nausea, headache, fatigue, dullness and thirst, even at very low concentrations [4,5]. Using gaseous air cleaners in non-industrial buildings also has the potential to save money by reducing sick building syndrome symptoms and improving work productivity [6].

During the last decades the chemical industry has shown a strong interest in developing clean and sustainable technologies [2]. The analysis of the applications of fiber materials for the chemical process industry to reduce polluting emissions shows that fiber catalysts have received considerable theoretical and experimental attention. These flexible materials have the advantage of being adaptable to different geometries, allow the regulation of permeability, are effective supports for the deposition of catalysts and can be applied in a wide range of temperatures [7]. An attractive approach for the preparation of a soft membrane with adsorption properties is the combination of molecular sieve porous materials (like zeolites) with a cheap and abundant organic matrix, such as natural cellulose. Once a stable zeolite/cellulose material is synthesized, paper filters can be obtained, and when thermal resistance is

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required, ceramic fibers can be used in combination with cellulose ones [4,8–10].

In this context, the main objective of this work is the preparation of Y zeolite-containing papers, their characterization and the evaluation of their performances as adsorbents for VOCs using toluene as a representative molecule. In order to extend the operation temperature range of the zeolite papers, the use of ceramic fibers along with cellulose ones was explored.

2. Experimental

2.1. Ceramic paper preparation

In order to obtain the zeolitic ceramic paper, two kinds of fibers were used: ceramic fibers (50 wt.% SiO_2, 48 wt.% Al_2O_3 and 2 wt.% impurities), obtained from a ceramic cloth from CARBO by elutriation, and cellulosic fibers obtained by repulping an industrial blotting paper produced from virgin softwood Kraft slightly-refined fibers. Ceramic fibers have an average length of 660 μm and an average diameter of 6 μm, whereas cellulosic fibers are 3 mm long and have a ribbon shape with an average width of 30 μm.

A papermaking technique with a dual polyelectrolyte retention system was used for which cationic and anionic polymers were employed. The cationic polymer was polyvinyl amine (PVAm) (Luredur PR 8095) from BASF, molecular weight 4×10^5 g/mol and charge density 4.5 meq/g and the anionic polymer was anionic polyacrylamide (A-PAM) from AQUATEC, molecular weight 10^4–10^5 g/mol and charge density 2.7 meq/g. Commercial NaY zeolite from Linde, Si/Al ratio equal to 3.5, was employed.

NaY zeolite (3.5 g) was added to a 500 ml solution volume of NaCl solution (0.01 N). Under soft agitation, 3.5 g of ceramic fiber, 3.5 g of cellulose and 33 ml PVAm solution (9 g/l) were incorporated. After 3 min of agitation, 21 ml A-PAM polymer solution (0.39 g/l) was added. With this suspension, a sheet was structured by the SCAN standard method [11] using water of 180 mS of conductivity and applying the double of the usual pressing pressure. The wet sheet was dried at 105 °C during 24 h and finally calcined in air for 2 h at 600 °C. The paper thus formed was called zeolitic ceramic paper, "PCer Z".

Following the same procedure other papers were prepared: A paper with all the above-mentioned ingredients but without the addition of zeolite, called "PCer", a paper with all the above-mentioned ingredients but replacing ceramic by cellulose fibers, called "PCel Z" and a cellulose paper (replacing ceramic by cellulose fibers and without zeolite) denominated as "PCel". Fig. 1 schematizes the preparation procedure. It is important to remark that papers denoted as "PCer" and "PCer Z" (ceramic papers) were calcined at 600 °C but those denoted as "PCel Z" and "PCel" (cellulosic papers) were only air-dried under papermaking standard conditions (23 °C-50%RH).

2.2. Physicochemical and mechanical characterizations

2.2.1. Airflow resistance

The sheet porosity was evaluated by determining the air resistance of the catalytic papers by measuring the time for a given volume of air to flow through the sheet. For this purpose, a Gurley-Hill, SPS tester was used.

2.2.2. Tensile strength

An INSTRON 3344 universal tester, with reference standard TAPPI T494-01 om was used.

2.2.3. Optical microscopy

The morphological aspects of the papers were examined using a Leica Stereozoom DM500 stereomicroscope.

2.2.4. Scanning electron microscopy (SEM)

A SEM Jeol JSM-35C equipment was employed operated at 20 kV acceleration voltage. Samples were glued to the sample holder with Ag painting and then coated with a thin layer of Au in order to improve the images.

2.2.5. XRD characterization

Crystalline phases were determined with a Shimadzu XD-D1 instrument with monochromator using Cu Kα radiation at a scan rate of 1°/min, from $2\theta = 5°$ to 50°. The pieces of about 2 cm × 2 cm were supported in a special sample holder designed for the XRD analysis. The software package of the equipment was used for the phase identification from the X-ray diffractograms.

2.2.6. TGA–SDTA

The thermal behavior of the ceramic papers was studied in a Mettler Toledo TGA/SDTA 851 instrument. The weight changes and the differential thermal process of the catalytic ceramic papers (10 mg of samples) were analyzed from 25 to 1000 °C with a heating rate of 10 °C/min in air flow (80 ml/min).

2.2.7. Textural properties

Nitrogen adsorption–desorption isotherms were obtained at −196 °C on a Quantachrome Autosorb 1C instrument. Previously, samples were outgassed at 105 °C for 2 h under vacuum. The

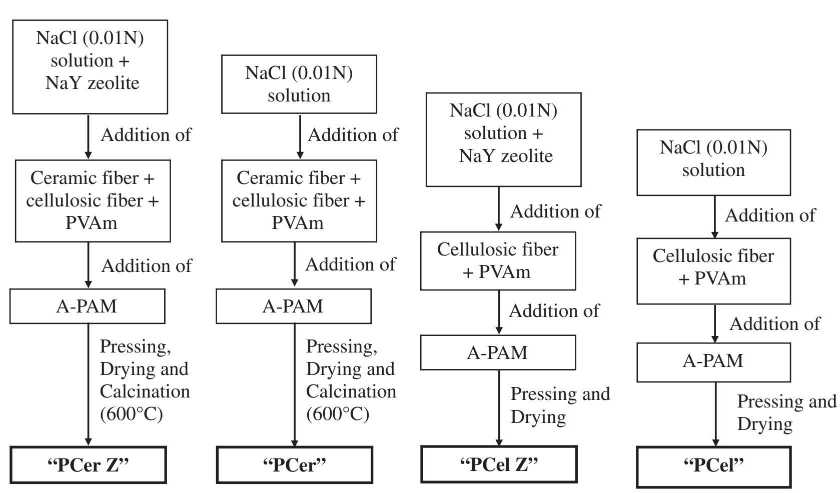

Fig. 1. Scheme of the catalytic paper preparation.