Research paper

Introduction of aluminum to porous clay heterostructures to modify the adsorption properties

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ABSTRACT

Porous clay heterostrucures (PCHs) are clay mineral based porous materials that have been mainly prepared by intercalation of structures with silica pore walls. In the present work the silica composition of the pore walls was modified by incorporating aluminum oxide, by a co-condensation methodology. Samples were characterized by nitrogen, water and toluene adsorption measurements. For the latter, heats of adsorption were measured using microcalorimetry. Characterization was also made by XRD, FTIR and chemical analysis by ICP and SEM-EDS. The materials were tested towards their selective adsorption properties, using chromatographic separation of toluene/n-heptane and toluene/cyclohexane mixtures. The amounts of aluminum that were introduced in the PCHs by the co-condensation methodology without disrupting the porous structure were limited but, still, they were able to modify the selective adsorption properties of the samples. Above a certain value it produces disruption of the pore structure.

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1. Introduction

In the last decades, porous clays have been developed for a wide range of applications, from heterogeneous catalysis to the separation and purification of gases and vapors (Ding et al., 2001; Gil et al., 2008; Pinto and Pires, 2010). These materials are usually prepared from natural clays, widely available around the world in soil deposits, and can thus be viable and ecological alternatives to produce adsorbents and catalysts or catalyst supports. Natural clays are hydrous aluminosilicates with small amounts of other compounds (iron or magnesium oxides), are classified in different groups (Grim, 1968; Velde, 1992) and have particle dimensions of less than 2 μm. They have no permanent porosity, but the expandable 2:1 group of clay minerals (Grim, 1968; Velde, 1992) has been used to synthesize pillared interlayered clays (PILCs) (Gil et al., 2000, 2008). PILCs were the first type of modified clay materials to have a permanent porosity and typical surface areas that may reach 350 m^2 g^{-1} which make them useful adsorbents in different applications. They are prepared by cation exchange with polyoxycations, followed by calcination. Recently, porous clay heterostructures (PCHs) have been reported (Galarneau et al., 1995; Polverejan et al., 2000; Pichowicz and Mokaya, 2001; Nakatsuji et al., 2004). These are mesostructured intercalates with surface areas reaching 800 and 1000 m^2 g^{-1}, obtained by the polymerization of silica sources, within the clay mineral layers, using an interlayer template approach. In the present work, we also introduced aluminum sources to study the effect on the adsorption and surface properties of the obtained PCHs.

The more common silica source used to prepare PCHs is tetraethoxysilane, although other silanes, such as phenyl or methyltriethoxysilanes, may be used (Nakatsuji et al., 2004). The surface of the pores may be modified by post-synthesis reaction of the reactive silanol groups to change the surface properties of these materials (Polverejan et al., 2000; Nakatsuji et al., 2004; Ferreira et al., 2006). The adsorption properties can thus be tailored for particular applications via the design of the pore size and the chemical nature of the surface, for example, for the adsorption of volatile organic compounds (Ferreira et al., 2006), for modifying the hydrophobic properties (Pires et al., 2008a) and for enhancing the separation of carbon dioxide from other components of natural gas (Pinto et al., 2008).

Another possibility for modifying the chemical surface of the pores, followed in this work and less explored in the literature, is the incorporation of other oxide sources (besides silica) during the synthesis of the PCH materials. In this work, we prepared PCHs with silica pore walls but the silica composition of the pore walls was modified by incorporating aluminum oxide in the synthesis. Among the most studied oxide species used for pillaring, i.e. silica, alumina or zirconium oxides, the aluminum oxide was chosen because it is the most used for preparing PILCs and produce materials with much higher surface acidity than pure silica (Gil et al., 2008, 2010). From preliminary work developed in our group, it was known that the synthesis of PCH materials with

only aluminum oxide sources leads to materials with low surface area, compared to what happens when silica sources such as tetra-ethylorthosilicate are used (Galarneau et al., 1995; Polverejan et al., 2000; Pichowicz and Mokaya, 2001; Nakatsuji et al., 2004). The approach followed in the present work was to use the silica procedure and to introduce a source of aluminum oxide in this procedure. The preparation of porous clay heterostructures with aluminum species in the silica walls by a co-condensation methodology is presented, to our knowledge, for the first time in this work.

PILCs have been studied in the last years for the adsorption of gases and vapors (Yang and Baksh, 1991a,b, 1992; De Stefanis et al., 1994; Yang and Cheng, 1995; Bandosz et al., 1996; Yang and Cheng, 1997; Ding et al., 2001; van Santen et al., 2001; De Stefanis et al., 2006; Lopez-Cortes et al., 2008). In recent works, we have studied the influence of the chemical nature of the oxide pillars on the separation of gases and vapors (Pires et al., 2008b). However, such influence is scarcely studied for PCHs, particularly with walls made of other oxides besides silica. Only recently, the influence of zirconium oxide on the separation of hydrocarbon mixtures with PCHs was presented by us (Pinto et al., 2012). We show here that the use of aluminum oxide sources during PCH preparation can be an interesting alternative to modify adsorption properties of these materials. Besides the porosity and structural characterization, the PCH materials with aluminum oxide were characterized for the hydrophilic properties (water adsorption), surface acidity using adsorption microcalorimentry and selectivity on hydrocarbon separation. The results revealed that these adsorption characteristics are dependent to some extent on the amount of aluminum oxide incorporated on the PCHs.

2. Experimental

2.1. Materials

The preparation of the porous PCHs was made using a Portuguese clay, from soil deposits in Benavila (Portugal), previously characterized (Pires et al., 1996). From the fraction <63 μm carbonates were removed by acid treatment and washing, in a dialysis tube, until a conductivity lower than 1 mS m^{-1} was attained. The PCH preparation method was based on the literature and was previously optimized (Galarneau et al., 1995; Polverejan et al., 2000; Pichowicz and Mokaya, 2001; Nakatsuji et al., 2004). A dispersion of the clay mineral (1 g in 100 mL of water) was equilibrated with 4.8 cm^3 of a 0.5 mol dm^{-3} cetyltrimethylammonium bromide, CTAB (Aldrich), solution with stirring overnight at 50 °C. The solid was then separated from solution by centrifugation and washed with demineralized water until neutral pH and air-dried. To the obtained solid, 5.3 cm^3 of decylamine (Aldrich, 95%) was added with 20 min stirring. A mixture of oxide sources was used: 35.5 cm^3 tetraethyl orthosilicate TEOS (Aldrich, 98%) for silica and variable amounts of aluminum isopropoxide, (Aldrich, 98%) for aluminum oxide. The solid was stirred for 3 h and was then centrifuged and air-dried overnight. The samples were calcined at 650 °C for 5 h, with a heating ramp of 1 °C min^{-1}. The samples were prepared with a nominal composition of 0.010, 0.015 and 0.020 mol of aluminum isopropoxide per mole of TEOS, and were labeled as 1Al, 1.5Al and 2Al, respectively. One sample was prepared without aluminum and was labeled 0Al.

2.2. Methods

Powder XRD was obtained in a Philips Analytical PW 3050/60 X'Pert PRO (θ /2θ) apparatus, with a X'Celerator detector. The diffuse reflectance infrared Fourier transform (DRIFT) spectra were collected on a Nicolet 6700 FTIR spectrometer at 4 cm^{-1} resolution using the Smart Diffuse Reflectance accessory, at room temperature with a DTGS TEC detector. Each collected spectrum was an average of 512 scans of the sample subtracted by the average of 128 background scans. Bulk chemical analysis was made by ICP at the "Laboratório of Análises of

IST", Portugal and chemical surface analysis was made by scanning electron microscopy with wavelength-dispersive spectroscopy (SEM–WDS) on a JEOL JXA-8200 microprobe.

Low-temperature nitrogen (Air Liquid, 99.999%) adsorption isotherms were determined in a volumetric automatic apparatus (Quantacrome, Nova 2200e), at −196 °C using a liquid nitrogen cryogenic bath. The samples, between 50 and 100 mg, were outgassed for 2.5 h at a pressure lower than 0.133 Pa. The degassing temperature was 300 °C for all samples.

The adsorption isotherms of water were determined at 30.0 ± 0.1 °C in an automated apparatus, model Omnisorp 100cx (Coulter, USA), using a fixed vapor dosing method. The outgassing conditions for all samples were similar to those used in the case of the nitrogen adsorption. The amounts adsorbed on an empty cell were used to correct the data of the adsorption isotherms.

Heats of adsorption were measured in a Tian–Calvet type microcalorimeter (BT, Setaram, France). In these experiments, the amounts adsorbed were determined in a volumetric apparatus, coupled to the microcalorimeter, equipped with a pressure transducer for the 0–133 kPa range (Baratron 310, MKS, USA). Before experiments, the samples of about 50 mg were outgassed overnight at 400 °C in a vacuum better than 10^{-3} Pa. Reproducibility in the determination of the amounts adsorbed was better than 0.2 μmol and the resolution of the calorimeter was 0.1 mW. Small doses of toluene were successively added at increasing pressures, simultaneously measuring the amount adsorbed and the heat evolved. After correction for the so-called heat of compression, the isosteric heats of adsorption, q^{st}, were calculated. The values of q^{st} obtained from calorimetric experiments can then be directly compared with those obtained from a family of adsorption isotherms at different temperatures (Guil et al., 1994). In this way, the volumetric isotherm, n^{ads} versus p, and the differential calorimetric isotherm, q^{st} versus n^{ads}, were obtained.

The adsorption and separation of hydrocarbon mixtures (n-hexane, cyclohexane and toluene) were studied by chromatography, at 120 °C and 150 °C. The separation factors were determined in a gas chromatograph (Hewlett Packard, 5890A) by the ratio of the retention times in a 100 mm × 3.2 mm stainless steel tube, using helium (Praxair, 99.999%) as carrier gas at 20 mL/min (mass flow controller; McMillan 80D Mass FLO-METER) and a thermal conductivity detector at 130 °C. The column with the materials was prepared with 80 to 120 mg of sample powder determined by weighing the column (Mettler, AE240). The materials were initially degassed inside the column, at 250 °C for 2 h, with a helium flow of 30 mL/min. The hydrocarbon mixture, about 0.1 μL, was manually injected in the gas flow using a syringe (Hamilton, 7001 N) and a standard injection port at 150 °C. At least two determinations of the retention times were done by repeated injections and the average value is reported. The selectivities were calculated using the adjusted retention time, by correcting for retention time of the peak of air. Typical difference in repeated selectivity determinations was 0.1.

3. Results and discussion

3.1. Textual and structural characterization

Porosity of the prepared PCH was assessed by nitrogen adsorption, at −196 °C (Fig. 1). The isotherms of the PCH prepared with aluminum oxide precursor are similar to the PCH prepared without aluminum oxide precursor (0Al), except for the sample prepared with more aluminum (2Al) where a significant decrease in the adsorption amounts is noted. The pore-size distributions (obtained using a DFT model for porous clays (Olivier and Occelli, 2001)) of the samples 1Al, 1.5Al and 2Al are similar to 0Al, which means that pore sizes are not much affected by the aluminum oxide precursor over the studied concentration range (Fig. 1). Nevertheless, as depicted in Fig. 1, two types of pores seem to exist. A set of smaller pores, with a maximum in the range of 1.3–1.4 nm (Type A) and a group of more heterogeneous porosity,