



Characterization and catalytic properties of porous clay heterostructures from zirconium intercalated clay and its pillared derivatives



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ABSTRACT

The insertion of zirconium or aluminium species into porous clay heterostructures has traditionally been performed in two steps. The first step prepares the porous clay heterostructures, and then adding the metal elements during the synthesis constitutes the second step. Here, a novel method is described that reduced the use of organic surfactants and inserted zirconium directly into the silica framework of the porous clay heterostructures in one step. It consisted of preparing the zirconium tetrameric species intercalated clay mineral as a precursor followed by co-intercalation of dodecylamine and the silica source (TEOS). The derived pillared zirconia clays were used as well as the precursor to prepare PCH materials. The materials were characterized by XRD, FTIR, TGA, ²⁹Si MAS NMR and XRF. The XRF technique confirmed the presence of Zr in the PCH material prepared from the intercalated clay. Improvements in specific surface area (918 m²/g) and pore volume (0.801 cc/g) were achieved. The concentration of Brønsted acid sites was deduced from the thermal desorption of cyclohexylamine and reached a value of 0.989 mmol of protons/g. This value was higher than the concentration for either the starting intercalated clay mineral or the derived pillared clays. Stronger Brønsted acid sites were developed into the PCH materials, in addition to Lewis sites, even at 500 °C, as indicated by the desorption of pyridine as a probe molecule. These acid sites were strong enough to convert n-heptane to isomers and cracking products.

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1. Introduction

The demand for new types of solid acid catalysts has inspired scientists to search for novel catalysts with desired properties for specific applications and to improve those already in use. Several new types of such solids have been developed, including pillared clays, and zeolite-like structures. The principle of pillaring consists of large inorganic polyhydroxocation species of Al, Zr, Ti, Fe, and Cr (either pure or modified with other cations) intercalated into the clay interlayer, followed by thermal treatment in the temperature range of 300–700 °C [1]. Calcination consisted the important step to prepare pillared clays (PILCs) materials, it results to the dehydroxylation of intercalated pillaring species and their

transformation into oxide pillars, thus propping apart the layers of the clays and producing thermally stable rigid cross linked materials with a large surface area, a certain porous texture and acidity [2]. The properties of pillared clays depend upon several factors such as the preparation temperature, pH of pillaring solution, the method of intercalation, washing and drying steps [1,2]. New family of materials was introduced by Pinnavaia et al., in 1995 [3], called porous clay heterostructures (PCHs). These PCHs were prepared by the combination of the synthetic methodologies used for pillared layered structures (PLS) and mesoporous solids of MCM-41 type, where a surfactant (mainly an alkylammonium cation) was intercalated between the clay layers, followed by hydrolysis and condensation of a silica source such as TEOS. The surfactant molecules were removed by calcination in an air atmosphere at 550 °C. The resulting materials exhibited high surface area with uniform and specific pore sizes [4,5]. The PCHs were applied in different fields as catalysts, as the adsorption of pollutants and as sensors for

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biological molecules [6–9]. The PCHs exhibited none or small amounts of acid sites, originated from the intercalated silica and from the host clays [4]. The enhancement of acidity was achieved either by the acid treatment of the host clays prior the synthesis of PCHs [10] or by incorporation of heteroatoms into the silica species, such as Al, Ti, and Zr [11–13]. The latter was achieved by copolymerization of TEOS with Zr-ethoxide for separation of aromatic molecules [13]. Another method consisted by long time sol–gel process (10 days) of TEOS and Zr-propoxide in 1-popanol [14], thus it consumed time and generated chemical waste. Recently, novel procedure was proposed as an alternative way to prepare Al-PCH materials [15]. It combined the pillaring process and PCH synthesis. This method had led to a decrease in the amount of the organic surfactants used, thus reducing the chemical waste generated during the preparation of PCH materials. The aluminium pillaring species were prepared by hydrolysis of aluminium salt solution and a base solution at molar ratios below 3 [16], adding another time-consuming step. However, the preparation of the zirconia pillaring species does not require a hydrolysis process for the zirconium oxychloride [17], or nitrate solutions [18]. The $[\text{Zr}_4(\text{OH})_8(\text{H}_2\text{O})_{16}]^{8+}$ cationic species were already present in these solutions. In this report, we focus our interest on incorporating zirconium species into porous clay heterostructures in a short period of time, using intercalated zirconia clay and related pillared materials (Zr-PILCs) as a precursor for porous clay heterostructure (Zr PCHs) materials, reacted with dodecylamine (C_{12} amine) and tetraethoxide orthosilicate (TEOS) as a silica source. This method will reduce chemical waste, the use of organic surfactants and shorten the time of synthesis. These materials were characterized in detail by different techniques. The acidity was estimated by temperature desorption of cyclohexylamine as a probe molecule and by *in-situ* FTIR spectroscopy of pyridine. The catalytic activity of these materials will be tested by the hydro-isomerisation of n-heptane. This reaction has an environmental benefit in the sense of improving the octane number of the fuel and increasing the efficiency of car engines.

2. Experimental

The montmorillonite clay (Mt, stx-2) was obtained from the Source Clays repository at Purdue University (USA) and has a cation exchange capacity of 92 meq/100 g. It was used without further modification. The zirconyl nitrate dihydrate ($\text{Zr}(\text{NO}_3)_4 \cdot 2\text{H}_2\text{O}$), tetraethoxide orthosilicate (TEOS), and dodecylamine (C_{12} amine) surfactant were purchased from Aldrich. The chemicals were used without purification.

2.1. Preparation of intercalated precursors and Zr-PILCs

The intercalated clay (Zr-Mt) was prepared from a zirconyl nitrate dihydrate solution after ageing at 80 °C for 1 h, corresponding to a Zr/clay ratio of 6 mmol/g. Five grams of clay were added directly to the zirconium solution. The final mixture was stirred for further 1 h at 80 °C, to allow the intercalation reaction. The resulting slurry was cooled to room temperature, and the solid was recovered by filtration, washed repeatedly with deionized water, and then dried in air.

The precursor Zr-Mt was calcined in an air atmosphere in the temperature range of 300–900 °C for 4 h at a heating rate of 5 °C/min to obtain the zirconia pillared clays (Zr-PILCs). The pillared clays will be identified as Zr-Mt(X), where X represents the calcination temperature.

2.2. Preparation of zirconium-PCH (PZr-MtCH) materials

The PZr-MtCH precursor was prepared as follows: 1 g of the prepared Zr-Mt precursor was reacted with neutral amine (dodecylamine, $\text{C}_{12}\text{H}_{25}\text{NH}_2$, C_{12} amine) and TEOS at molar ratios of Zr-clay/ C_{12} /TEOS approximately 1/20/150. The mixture was then stirred for 4 h at room temperature. After the reaction, the product was recovered by filtration and air-dried overnight. The sample will be denoted as PZr-MtCH-prec.

The same procedure described above was also followed to prepare PCH precursors from pillared clays (Zr-Mt(X)). The samples will be designated as PZr-Mt(X)CH-prec, where X is the calcination temperature of the Zr-Mt precursor.

The PZr-MtCH or PZr-Mt(X)CH precursors were calcined at 550 °C in an air atmosphere for 6 h with a heating rate of 1 °C/min. The samples will be identified as PZr-MTCH or PZr-Mt(X)CH materials.

2.3. Characterization

The chemical composition of the pillared clays and PCH derivatives was determined using X-ray fluorescence (XRF) from a Bruker Model S4. The X-ray diffraction technique was used to examine the success of the pillaring process and the PCH synthesis. An X-ray diffractometer (advance 8) from Bruker was used for this purpose. FTIR spectra of the samples were measured by the KBr disk method over the range of 4000–400 cm^{-1} ; a Biolab instrument was used for the purpose. Thermogravimetric studies were carried out using equipment from TA Instruments (SDT2960). Approximately 20 mg of the sample was used, and the heating rate was maintained as 5 °C/min in an air atmosphere. ^{29}Si MAS (magic-angle spinning) NMR spectra were recorded on a Bruker 400 spectrometer, operating at a ^{29}Si NMR frequency of 78 MHz. 4-mm magic-angle-spinning (MAS) probehead was used with an 8.0-kHz sample-rotation rate. In all, 100 scans were performed with a recycle delay of 200 s. The ^{29}Si chemical shift is reported with respect to tetramethylsilane (TMS). The surface areas of all of the samples were determined by BET nitrogen adsorption at liquid nitrogen temperature using a Quantachrome Autosorb A6. The samples were degassed at 200 °C prior the measurements. The pore volume was measured by the uptake of nitrogen at a relative pressure of 0.97. The micropore pore volumes were evaluated using the *t*-plot method. Transmission electron microscope (TEM) micrographs were obtained from JEOL model JEM1400. Brønsted acidity (proton concentration) was determined using programmed temperature desorption with cyclohexylamine as a probe molecule. The TG measurements were carried out under dry nitrogen at a flow rate of 200 ml/min and a heating rate of 10 °C/min. The values are expressed per weight of clay at 290 °C to exclude any differences in the amount of physisorbed base or non-exchanged interlamellar water. The weight loss between 290 and 420 °C was used to compute the acidity in terms of mmol of cyclohexylamine desorbed. It was assumed that each molecule of the base interacts with one protonic acid site [15].

Pyridine was used as a probe molecule to differentiate between the different acid sites (Brønsted and Lewis sites). Fourier-Transform Infrared (FTIR) spectra of the chemisorbed pyridine were measured using a Nicolet 205 FTIR spectrometer. A 40- to 50-mg sample of material previously calcined in air for 4 h at 500 °C was pressed (for 2 min at 10 ton/cm^2 pressure under vacuum) into a self-supporting wafer 13 mm in diameter. The wafer was further calcined under vacuum (10^{-3} torr) at 500 °C for 2 h and then exposed to pyridine vapour at ambient temperature. While in the pyridine atmosphere, the wafer was heated at 100 °C for 1 h to allow the pyridine to permeate the sample. The wafer was cooled to

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