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Mesoporous iron phosphate/phosphonate hybrid materials

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ABSTRACT

Relatively high surface area pure mesoporous iron-phosphorus oxide-based derivatives have been synthesized through an S^+I^- surfactant-assisted cooperative mechanism by means of a one-pot preparative procedure from aqueous solution and starting from iron atrane complexes and phosphoric and phosphonic acids. A soft chemical extraction procedure allows opening the pore system of the parent as-prepared materials by exchanging the surfactant without mesostructure collapse. The nature of the pore wall can be modulated from iron phosphate up to hybrids involving approximately 30% of organophosphorus entities (phosphonates or diphosphonates). X-ray powder diffraction, transmission electron microscopy and surface analysis techniques show that these hybrid materials present regular unimodal disordered pore systems. Spectroscopic results (Fe-57 Mössbauer, XPS, UV–vis, FTIR and Raman) not only confirm the incorporation of organophosphorus entities into the framework of these materials but also provide us useful information to elucidate both the mechanism through which they are formed, and some details on their specific local structures.

1. Introduction

Nature created a diversity of open-framework inorganic materials with regular pore architectures [1,2]. Crystalline aluminosilicate zeolites were the first type of microporous materials to be recognized [3]. Academic and industrial interest in zeolites steadily progressed as chemists learned to synthesize them in the laboratory [3,4]. All known zeolite frameworks are based upon vertex-sharing (SiO_4) and (AlO_4) tetrahedra, which delimit interconnected channels or cages [2–4]. Because of their wide-ranging applications in fields where molecular recognition is needed [3], the attention paid to three-dimensional open-frameworks led to the search for new material families. Efforts were successful in the early 1980s, when investigations at Union Carbide yielded a new class of crystalline molecular sieves, the aluminophosphates (ALPOs) [5]. With neutral tetra-connected frameworks (alternating [PO_4] and [AlO_4] units) closely related to those adopted by zeolites [6], ALPOs quickly stirred interest looking for expanding micropores availability. Due to their significant electronic and structural similarities, ALPOs chemistry evolved through similar ways to that of zeolites and tackling also questions as, among others, the chemical modification ("functionalization") of the material walls or the "expansion" of the pore sizes [7].

In the broad sense, ALPOs chemistry has proven to be more complex (or versatile) than that of silica-based materials. So, ALPOs formally allow even a complete exchange of aluminum atoms or phosphate groups by other metal atoms or phosphate-related entities, respectively. In fact, a diversity of new inorganic open-framework aluminum-free phosphates was characterized during the 1990s [2]. The well known structure-directing effect due to small organic molecules was key for synthesizing such porous materials, although collapse of the inorganic framework after "template" removal often occurred [2]. At the same time, replacement of phosphate groups by other tetrahedral or pseudotetrahedral entities was explored for preparing new open structures, what also made possible the obtaining of inorganic–organic hybrid skeletons (looking for overcome limitations imposed by the relatively small sizes of the polyhedral centers and their connectivity in purely inorganic systems). With regard to the "expansion" of the pore sizes (in the search for efficiency in treatments of bulky substrates), the Mobil' synthesis of the M41S silicas by using surfactants as "supramolecular templates" constituted a milestone in the field by offering a way for expanding the typical pore sizes in zeotypes to the mesopore range [8,9]. Such strategy was quickly adapted for synthesizing also non silica-based materials, although

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it met with limited success [10]. In that concerning ALPOs and related phosphates, to imitate the chemistry of mesostructured/mesoporous zeolites did not result as straightforward as initially might be thought precisely because of the relative chemical versatility of non-silica materials [11]. In practice, concerning phosphate chemistry, the area most widely explored in last decades has been, very likely, that dealing with organically modified inorganic open-frameworks [2,12–14]. In order to get open skeletons, phosphate-like moieties have been replaced (totally or in part) by more complex related organic species (mono or diphosphonates, functionalized monophosphonates, mixed phosphate–oxalate groups, and so on). It does not seem hasty to state that in the many and ingenious work devoted to these hybrid materials lays the genesis of the nowadays exciting metal–organic frameworks (MOFs). The state of the art of phosphonate-based MOFs (including also non-crystalline or unconventional UMOF materials) has been recently reviewed by Clearfield and co-workers [15].

In previous publications, our group reported on the synthesis of organically modified pure mesoporous ALPOs [16–19]. Together with Al, the preparation of micro or mesoporous phosphate–phosphonate hybrid materials is well documented for Ti and Zr, and there is also information concerning related materials including a diversity of metals (like Ga, In, Sn, V, Mo, Fe, Co and Zn) [2,11]. In particular, iron phosphates have aroused interest because of both their very rich crystal chemistry and traditional or novel (based on surface and diffusion phenomena) practical applications [20–23]. In fact, there is a large variety of naturally occurring iron phosphate materials, which includes many structurally diverse examples of both open and dense octahedral-tetrahedral frameworks [20,24]. The mineral cacoxenite, $[AlFe_{24}(OH)_{12}(PO_4)_{17}(H_2O)_{24}]\cdot 51\ H_2O$, constitutes a beautiful example of how nature constructs stable microporous solids: built up from isotropic Fe^{3+} cations in $Fe_4(OH)_2{}^{q+}$ clusters and $PF_{26}O_{28}{}^{q-}$ Keggin-like blocks, it contains relatively large cylindrical channels (free diameter size of 1.42 nm) filled with delocalized water molecules [25]. Looking to imitate nature, the application of hydrothermal techniques and the generalization of the use of small molecules as structural directing agents, allowed preparing a wide set of layered and open structures based on iron phosphate frameworks [2,20]. However, as suggested above, utilization of micelles as "supramolecular templates" for obtaining high surface mesoporous iron phosphates has not resulted so satisfactorily because of the intermediate formation of lamellar or other unstable phases, which readily collapse by elimination of the surfactant. Thus, the only apparently successful synthesis reported until now is based on using an anionic surfactant (dodecyl sulfate) as template under the obligatory assistance of HF [26,27]. In the self-assembling processes leading to the mesostructured intermediate, the dodecyl sulfate portions should be able to match with fluoride-linked iron-phosphate cationic clusters, and subsequent surfactant removal occurs without collapse of the mesophase. Also, a related dodecyl sulfate directed procedure (excluding HF) allowed obtaining a hybrid mesoporous iron oxophenyl-phosphate material under hydrothermal conditions [28], although the P:Fe molar ratio of 0.47 in this solid is far from that corresponding to the 1:1 ideal stoichiometry. In contrast, as far as we know, all attempts based on using surfactants of different nature (including cationic ones) only have rendered mesostructured solids which do not resist template elimination [29].

In this paper, we report on a detailed study of the one-pot surfactant-assisted procedure that has allowed us to prepare for the first time mesoporous iron phosphates with organically modified surfaces and/or frameworks by using a cationic surfactant as template. This simple and reproducible method yields pure large surface area mesoporous materials displaying high chemical homogeneity as well as good dispersion of the organic groups. On the basis of spectroscopic results, we analyze the iron–oxygen and phosphorus–oxygen local environments and, additionally, we present here a reasonable proposal accounting for the self-assembly mechanism of formation of these hybrid materials.

2. Experimental section

2.1. Chemicals

All the synthesis reagents are analytically pure and were used as received from Aldrich ($FeCl_2{\cdot}4H_2O$, triethanolamine [$N(CH_2{-}CH_2{-}OH)_3$, hereinafter TEA], cetyl-trimethylammonium bromide (CTMABr), and phosphoric acid) and Fluka (methylphosphonic acid, 1,2-ethylenediphosphonic acid)

2.2. Preparative procedure

The method is based on the use of a cationic surfactant (CTMABr) as supramolecular template and porogen agent (after template removal), and a hydroalcoholic reaction medium (water:-TEA). As commented below, the presence of the complexing polyalcohol is basic in order to harmonize the rates of the hydrolytic reactions of the iron species in water–phosphoric acid media and the subsequent processes of self-assembling among the resulting inorganic polyanions and the surfactant aggregates.

In a typical synthesis leading to sample 3 (a mixed phosphate–phosphonate iron mesoporous material), $FeCl_2{\cdot}4H_2O$ (1.23 g) was slowly added at 60 °C to a mixture of TEA (33 mL) and NaOH (0.56 g). The resulting solution was heated under air at 120 °C, and CTABr (2.25 g) was added and dissolved without apparent alteration. After cooling this solution until 60 °C, it was mixed with methylphosphonic acid (5.80 g) and water (100 mL). The color of the surfactant-containing solution evolved from green to red as the formation of iron-pseudoatrane complexes (Fe(III) compounds containing TEA-based ligands) advanced [30]. Finally, H_3PO_4 (5%) was added drop by drop with the help of a burette while controlling the apparent pH value. The solution was gradually decolorized, and we stopped the addition of H_3PO_4 (12.1 mL) as soon as some turbidity was observed (apparent pH value slightly below 6). After a few minutes, a beige colored solid appeared. The resulting suspension was aged at room temperature for 12 h, filtered off, washed with water and ethanol and air dried. The surfactant was chemically extracted from the mesostructured powder with an acetic acid/ethanol solution (*ca.* 1 g of powder, 16 mL of acetic acid and 130 mL of ethanol; $t = 24$ h, at room temperature). The final mesoporous material was separated by filtration, washed with ethanol and air dried. A completely equivalent procedure was followed for obtaining solids containing terminal (methylphosphonate) or bridging phosphonates (1,2-ethylenediphosphonic acid). In all cases, the molar ratio of the reagents was adjusted to 0.2 Fe: 7.7 P (H_3PO_4 + Phosphonic acid): 7 TEA: 0.5 NaOH: 0.22 CTMABr: 180 H_2O. Summarized in Table 1 are the main synthesis variables and physical data concerning the materials prepared in this way: pure iron phosphate (sample 1), mixed iron phosphate–monophosphonate solids (samples 2–4), and mixed iron phosphate–diphosphonate derivatives (samples 5–7).

2.3. Physical measurements

All solids were characterized by elemental CNH analysis and electron probe microanalysis (EPMA) using a Philips SEM-515 instrument (to determine Fe and P). P/Fe molar ratio values averaged from EPMA data corresponding to *ca.* 30 different particles of each sample are summarized in Table 1. X-ray powder diffraction (XRD) data were recorded on a Seifert 3000TT θ–θ diffractometer using Cu Kα radiation. Patterns were collected in steps of