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ARCILLAS PILARIZADAS: UN PROYECTO DE SÍNTESIS INORGÁNICA EN EL LABORATORIO

PILLARED CLAYS: A PROJECT OF INORGANIC SYNTHESIS IN THE LABORATORY

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Abstract

The present paper shows the pillaring process of a natural montmorillonite-type clay, emphasizing that this inorganic synthesis can be used as an interesting science experiment to be incorporated in the laboratory activities of Inorganic Chemistry or Materials Science courses. To carry out the proposed experimental work we suggest to use a problem-solving educational methodology founded in the constructivism, and named inquiry-based instruction strategy with open-ended inquiry experiment style. Finally, a detailed synthesis procedure and the verification of the mineral intercalation-modification by X-ray diffraction are shown.

Keywords: Inorganic chemistry, problem solving, inquiry-based laboratory, pillared clay.

Resumen

El presente artículo muestra el proceso de pilarización de una arcilla natural tipo montmorillonita, enfatizando el posible uso de esta síntesis inorgánica como un experimento interesante que puede ser incorporado en las actividades de laboratorio propuestas para cursos de Química Inorgánica o de Ciencia de Materiales. Para desarrollar el trabajo experimental propuesto se sugiere una metodología basada en el constructivismo: la resolución de problema, denominada específicamente como estrategia de enseñanza basada en la investigación, en estilo abierto. Finalmente, se muestran el procedimiento detallado de la síntesis y la verificación de la intercalación del mineral mediante difracción de rayos-X.

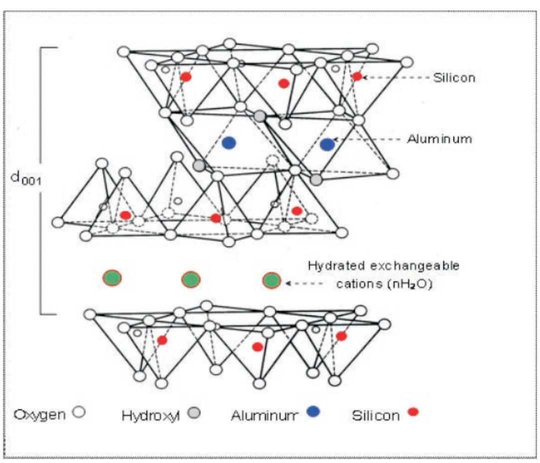
Palabras claves: Química inorgánica, resolución de problema, laboratorio basado en investigación, arcilla pilarizada.

Introduction

The clay minerals

Clay minerals are layered aluminosilicates materials built from the association of tetrahedral entities of silicates and octahedral sheets in which, an Al^{3+} or Mg^{2+} cation is surrounded by six hydroxyl groups or oxygen atoms, with possible isomorphous substitutions in the octahedral sheet and in the tetrahedral one (Moore and Reynolds 1997; Newman and Brown 1987). Among the clay minerals, smectites or montmorillonites (graphic 1) are present, which are characterized by a moderate interlayer charge fraction with good expansion capacity, which permits them to be swelled when they are immersed in aqueous media and modified by pillaring-intercalation with voluminous chemical species.

Graphic 1. Structure of a 2:1 clay mineral (type smectite).

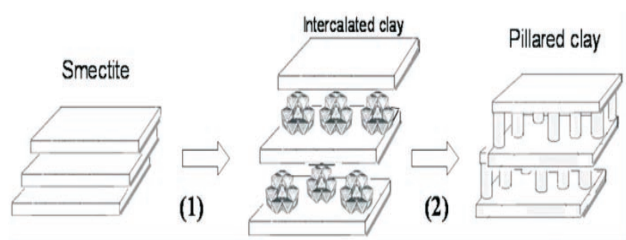


On the other hand, clay minerals have enormous importance in industry (ceramic, paper, chemical, pharmaceutical and petrochemical industries) and in everyday life (tiles, bathroom accessories, cosmetic products, detergents, foot talc, etc.), but knowledge of these minerals is generally not taken into account in the curricular programs designed for Inorganic Chemistry in the Chemistry degree. However, The Clay Mineral Society recently emphasized the need to incorporate this knowledge in the curriculum as an introductory theme and they recommend harmonious integration of Learning Theory (Constructivist focus, Learning Cycle and the Benchmarks for Scientific Literacy) with clay-science teaching (Rule 2002).

What are pillared clays?

The pillaring procedure is based on the introduction (by ion exchange) of an inorganic polyhydroxocationic species (for example, aluminium keggin ion: $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$) in the interlayer space (intercalation), which after being washed, dried and calcined yields the pillared material (Gil et al. 2000; Kloprogge 1998). During calcination the metallic polyhydroxocation produces a nano-oxide (oxide nanoparticles) that props apart the layers and is strongly fixed to the clay surface. Such oxide is called a "pillar" and the final material is the "pillared clay" (graphic 2).

Graphic 2. Scheme of the pillaring-intercalation process with the aluminum polyhydroxocation (keggin): (1) Intercalation by ion exchange with polyhydroxocation, (2) formation of pillars by calcination.



The application fields of these materials are wide due to the possibility to intercalate different types of pillars, making them appropriate to specific processes of adsorption, molecular separation, or heterogeneous catalysis in a broad range of reactions (Centi and Perathoner 2008; Gil et al. 2000): hydrogenation-dehydrogenation, esterification, epoxidation, alkylation, isomerisation, and reactions of environmental impact such as the oxidation of organic pollutants in aqueous media and the oxidation of carbon monoxide or volatile organic compounds in the gas phase. However, the pillaring of clay minerals, an important and easy synthesis of inorganic materials, is not commonly implemented in the development of inorganic programs or related basic courses; for that reason in the present paper we attempt to give the basic orientations for this synthesis employing "inquiry-based learning" as a pedagogical strategy.

Pedagogical focusing

Laboratory projects by inquiry-based instruction

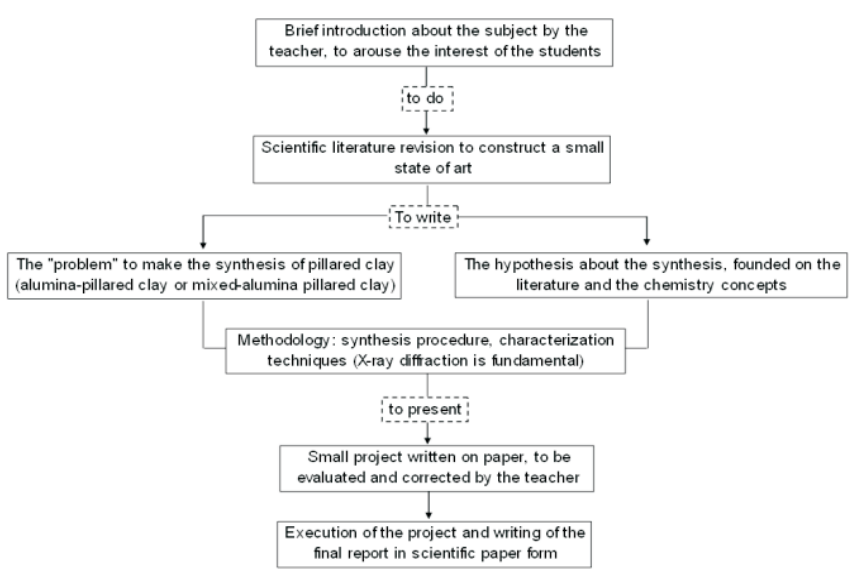
Several different work styles exist to teach sciences in the laboratory, but perhaps a cooperative construction of knowledge is better reached by developing mini-projects. In Science Education the general term project (or mini-project) is referred to the practical work in which the students employ several weeks (for example 4-5 weeks with laboratory sessions of 3-5 hours) to accomplish the proposed topic (Mc Donnell et al. 2008; Mohrig et al. 2007). On the other hand, *inquiry-based learning* strategy, is a teaching methodology founded in the *constructivism*, that involves a *problem solving* approach (Mohrig et al. 2007; Pozo and Gómez, 2001; Sanger, 2008) and represents one of the best methods to understand the *nature of science* (term used to describe the way that science is done and the way that scientific knowledge is constructed (Sanger, 2008). Currently inquiry-based instruction constitutes a line of research in Science Education, in which it is proposed to develop a set of curricular contents through an activities series and "problematical situations" initiated on questions of interest to the students, which encourage them to reconstruct their own knowledge. In the context of inquiry-based learning, the *open-ended* instructional style suggests that the practical work can be developed by a laboratory-investigative approach. Questions raised in the course of projects with this experimental educational style represent a good approach to scientific work; they permit theoretical concepts to be related to some practical applications and help to transfer school knowledge to everyday contexts (Pozo and Gómez, 2001).

In the open-ended style of inquiry-based learning, similar to the scientific work, the student acts like a "researcher" (under activities oriented by the teacher) and must not have a lab-guideline (cookbook), but he should construct or adapt his own procedure using chemistry literature. The student must delimit the problem, construct hypotheses founded in scientific literature, design experiments, obtain coherent results, and show his ability to analyze results and situations. However, these aspects could not be easily reached at any educational level, but this can be an advanced stage of the implementation of this learning model in which, in the case of science students and particularly of chemistry, the learner requires some typical experimental competences to make, adjust, manipulate, and to correctly direct the chemistry experiment toward verification of the hypotheses. In this learning model the teacher acts as a director of research, who manages the work generating pertinent inquiries, giving coherent and opportune explanations, suggesting and facilitating the implementation of techniques and methods of work. In addition, the teacher discusses the results with the students and he stimulates the accomplishment of oral and written reports (seminaries, posters sessions and final reports in the scientific paper form).

Methodology and activity

In principle a representation of work is proposed in graphic 3, based on general recommendations for a guideline-program of activities inside the method of inquired-based learning (Pozo and Gómez, 2001).

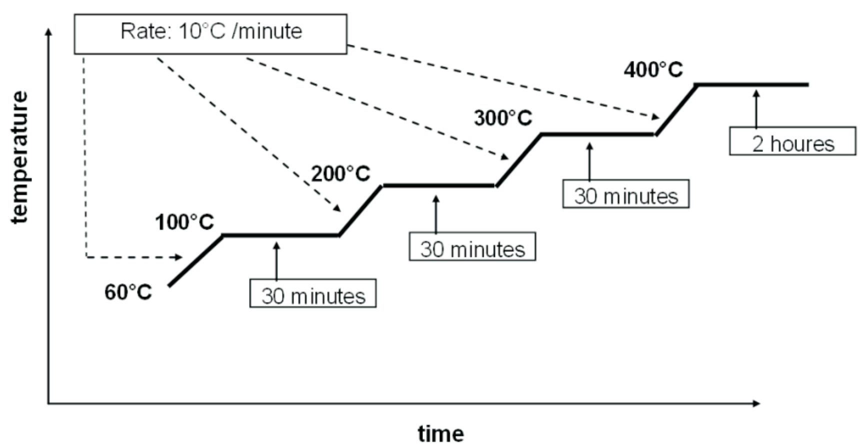
Graphic 3. Schematic representation of the main activities to carry out about the mini-project of synthesis of "pillared clays".



Next, the results of synthesis of a smectite pillared with aluminum oxide oligomers (alumina-pillared clay) are presented. The starting material was a montmorillonite-type clay from Valle del Cauca (Colombia) and commercialized by Bentocol Company (Colombia), previously separated by sedimentation in aqueous suspension to obtain the <2μm particle size fraction and then homoionized with a 1 N NaCl solution. To modify the clay an Al^{3+} polyhydroxocationic aqueous-solution (where keggin is the most abundant ion) was prepared from aluminum nitrate (Merck 95%), by slow addition (dropwise, ≈0.5 mL/min) of a 0.2 M NaOH solution (from Merck 99%) on the Al^{3+} (0.2 M) solution under vigorous stirring at room temperature, maintaining an OH/Al molar ratio equal to 2.2. The final solution was aged for two hours at 60°C.

The pillaring of clay was carried out by ion-exchange of this material with the Al^{3+} polyhydroxocationic solution previously aged (pillaring solution), using a ratio of 20 miliequivalents of Al^{3+} for each gram of clay. Consequently, the pillaring solution was slowly added (dropwise and under stirring) to an aqueous suspension (2% p/v) of clay (hydrated for 24 hours before used). After adding, the mixture was stirred for 3 hours at room temperature. The resultant material (intercalated solid) was washed several times by redispersing and centrifugation in distilled water until nitrate-free. The solid was dried at 60°C and finally calcined at 400°C in a furnace, using static air atmosphere and a heating ramp (from 60 to 400°C, and then at 400°C the solid is calcined for 2 hours) (graphic 4). The final solid is the pillared clay.

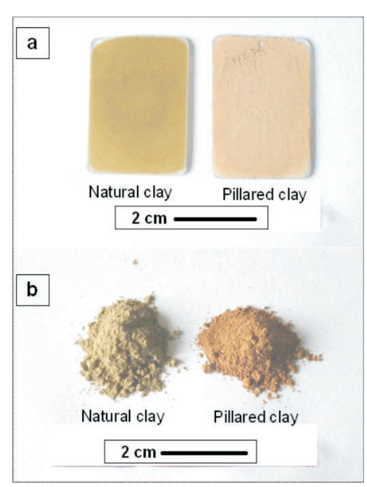
Graphic 4. Heating ramp designed for successful calcination of pillared clays.



Results

The natural clay and alumina-pillared clay were analyzed by X-ray diffraction (XRD) using the oriented-film technique. Graphic 5a shows the oriented-films of the solids obtained by deposition of a few drops of an aqueous suspension of material on a glass slide, which finally is dried at room temperature and then at 60°C. Graphic 5b shows the physical appearance of natural clay and alumina-pillared clay after ground in mortar and passed through a sieve (ASTM # 60).

Graphic 5. Images of the (natural and pillared) clays. a) oriented films, b) powder.

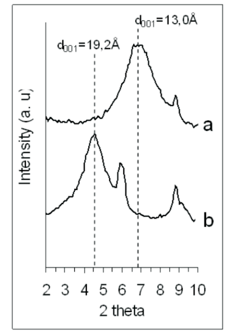


The results of X-ray diffraction (graphic 6) show an increase of the basal spacing (d_{001}) indicating that the pillaring process was successful (for clay minerals d_{001} is the peak located at lowest 2θ angle). Shift of d_{001} toward higher values is the unique effective characterization that permits confirmation of the pillaring-intercalation of clay minerals. To determine d_{001} values it is necessary to use Bragg's equation:

$$n\lambda = 2dsen\theta \qquad \text{(Equation 1)}$$

where λ is the wavelength of diffractometer (in this case λ=1.54056Å), d is the interplanar distance, θ is the diffraction angle, and n=1.

Graphic 6. Diffractograms of natural clay (a) and pillared clay (b)



Hazards

The students must check the technical-safety cart for every reactant to use. The furnace use and the accomplishment of heating ramp must be verified for the teacher. Additionally the X-ray diffraction analysis should be carried out by (or under inspection of) an expert-technical person.

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