Editorial

Catalytic Applications of Clay Minerals and Hydrotalcites

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1. Introduction

Clay minerals are the most abundant minerals on the surface of Earth. These minerals are well-known from the paleolithic period where the primitive person used clay minerals to produce ceramics or pottery. The number of uses and applications has been increasing as life has evolved. Nowadays, clay minerals are employed in a wide range of applications. Between them, their use is highlighted in the ceramic field as potteries, refractories, and porcelain, in rubber industry as fillers, in paper industry as fillers or coatings in the pharmaceutical field. Other interesting applications are as adsorbent and filter, drilling fluids of deodorizing agent, catalyst, catalytic support among others. In an elemental classification, the clay minerals can be grouped as cationic clays, which are very common in nature, and anionic clays, which are rare in nature although the cost for their synthesis is relatively low [1,2]. Considering the structural and morphological composition of cationic and anionic clays, this editorial is focused on the use of these clay minerals for catalytic applications, highlighting the possible modifications of its structure to improve its catalytic behavior.

2. Cationic Clays

Among clay minerals, phyllosilicates are the minerals that have received the most attention due to their chemical composition and textural properties. Phyllosilicates are lamellar silicates which are composed by tetrahedral sheets $[MO_4]^{4-}$, where M can be Si^{4+}, Al^{3+} or Fe^{3+}, and octahedral sheets which are connected through sharing edges. The partial substitution of Si^{4+} by Al^{3+} in the tetrahedral sheets and the partial substitution of Al^{3+} or Fe^{3+} by Mg^{2+} in the octahedral sheets generate a deficiency of positive charge, which is counterbalanced by the incorporation of alkaline or alkaline-earth cations in the interlayer spacing between adjacent sheets [3]. These phyllosilicates display both Lewis and Brönsted acid sites on the edge of these sheets. Thus, Brönsted acid sites are attributed to the external hydroxyl groups while Lewis acid sites are ascribed to the partial substitution of Si^{4+} by Al^{3+}. The acidity on the surface decreases according to water adsorbed on the clay increases [4]. Besides acid sites, the presence of Fe^{3+} ions in the edges of the sheets can also provide electron-accepting or oxidizing sites [5]. In the same way, the redox behavior of the clay minerals can be modified by the substitution of the alkaline or alkaline-earth cations located in the interlayer spacing by other cations such as Ag^+, Cu^{2+} or Fe^{3+} [6]. However, in many cases, the amount of available active sites is very limited. It has been reported in the literature that the interlayer spacing is between 7Å and 14Å in such a way that most of the molecules cannot access all active sites, so the only active centers available are those located on the outer surface [7].

It has been reported in the literature that the specific surface area determined by the BET equation is ranged between 10–150 m^2g^{-1} [8]. In most cases, N_2 molecules cannot access the interlayer spacing, so the specific surface area is mainly ascribed to the interparticular voids [7]. In any case, the surface area is remarkable so that these phyllosilicates can also be used as catalytic supports to disperse a wide variety of active phases.

In this sense, the acid treatment of the phyllosilicates can increase the surface area because of a partial solution of the octahedral sheet [9]. This partial digestion is more pronounced in the case of Mg-rich phyllosilicates as saponites or sepiolite [10]. The acid treatment also produces a higher amount of acid sites due to the generation of partially coordinated Al^{3+}-species, forming Brönsted acid sites as well as the cationic exchange of the alkaline or alkaline-earth cations by H^+-species in the interlayer spacing [11].

The ability to change ions located in the interlaminar spacing by other bulkier ions provide some phyllosilicates as smectites great potential in the field of catalysis as pillared structures may be formed with a specific surface area much higher than the starting materials. In this sense, the substitution of Na^+ by oligomeric (hidr)oxy aluminum cations provokes an increase of the interlayer spacing. In the next step, a thermal treatment favors the condensation between the silanol groups of the smectites sheets and the -OH groups of the oligomeric cations, leading to pillared clays (PILCs) [12]. Besides Al_2O_3 pillars, a wide variety of pillars have been synthesized from their respective polyoxocations. Between them, it can be highlighted the formation of Zr, Cr, Ti, Fe, Al/Ce, Al/Fe or Al/Co. The formation of these pillars can provide Lewis or Brönsted acid sites [13]. In addition, the increase of the surface area can allow for the use of these pillared clays as support, leading to bi-functional catalysts in many cases [13].

The synthesis of porous clay heterostructures (PCHs) is another alternative to obtain materials with high specific surface area [14]. The synthesis of PCHs consists in the substitution of the cations of the interlayer space by a bulky organic cation, which enhances the interlayer spacing. Then, silicon precursor in the form of alkoxide is polymerized around the organic cation, forming a silica structure between adjacent layers. Finally, the organic matter is removed under thermal treatment [15]. Through this synthetic strategy, it is possible to modulate the pore diameter according to the specific conditions of the catalytic reactions [15]. From this methodology, it is also possible to incorporate some heteroatoms in the pillars such as Al, Zr or Ti [16,17]. In these structures, Brönsted acid sites are observed in the sheets of smectite while Lewis acid sites are ascribed to the existence of Si-O-M bridges in the pillared structure. In addition, the increase of the specific surface area, modulated pore diameter and narrow pore diameter distribution allows its use of catalytic support [17].

Future perspectives for cationic clays could be based on the increase of the availability of sheets through a controlled delamination, the combination of organic–inorganic interactions, the deposition of nanoparticles, and the design of hierarchical structures, among others.

3. Anionic Clays

The number of natural anionic clays is fewer than that observed for natural cationic clays. However, these anionic clays also named hydrotalcites or layered double hydroxides can be easily and quickly synthesized in the laboratory [1]. This family of clays have also attracted the scientific community due to its wide range of applications in many fields such as medicine, biochemistry, electrochemistry, photochemistry, and polymers as additives. In addition, this material can also be used as an ion exchanger, an adsorbent, and a catalytic support or catalyst [18].

The most studied and best-known anionic clay are those composed by Mg^{2+} and Al^{3+} species. Its elemental base is composed of octahedrons, which are shared through their edges in such a way that each octahedron consists of one Mg^{2+} in the center of the octahedron and six OH^- on their vertexes. The partial substitution of Mg^{2+} by Al^{3+} causes a charge deficiency on the brucite sheet, which must be counterbalanced by the inclusion on anions, mainly $CO_3{}^{2-}$ in the interlayer spacing [18].

The structure of the anionic clays is not limited to Mg^{2+} and Al^{3+} species. Thus, Mg^{2+} cations can be partially or totally replaced by Cu^{2+}, Zn^{2+} or Ni^{2+}, while Al^{3+} cations can be partially or totally replaced by Cr^{3+} or Fe^{3+} [18]. Traditionally, anionic clays have been synthesized by co-precipitation method, although alternative methods such as mechanochemi-

cal, tribochemistry, microwave or sonication methods have been reported to obtain anionic clays with different crystallinity in the last years.

From a catalytic point view, anionic clays display poor catalytic behavior as a consequence to its basicity is very low, which is probably due to H_2O blocking the basic sites [19]. However, a thermal treatment causes dehydroxilation in the brucite sheets as well as the removal of CO_3^{2-} located in the interlayer spacing causes a collapse of its structure leading to their respective mixed oxides. The properties of the obtained oxides depend on M^{2+}/M^{3+} molar ratio and the chemical composition. Thus, the presence of MgO can provide basic sites while Al_2O_3 can provide acid sites. On the other hand, other oxides such as CuO or NiO are reducible in their respective metallic species. Considering the great variety of M^{2+} and M^{3+} species, it is possible to synthesize many polyfunctional catalysts from anionic clays [18].

The thermal treatment leads to the formation of small particles. This fact generates high porosity ascribed to the voids between particles, achieving a surface area between 100–300 m^2g^{-1} in such a way that the obtained oxide can also be employed as catalytic support.

The lamellar structure of the anionic clays can also form pillared structures due to the substitution of the CO_3^{2-} by a bulkier anion such as isopolyanions, heteropolyanions or ferro/ferricyanides. However, the formation of these pillars are not easy, as the anionic exchange capacity is more complex than that observed in cationic clays since the hydrolysis between the -OH groups and the anion can also collapse the layered structure or the low stability of the anionic clays [19]. Considering these disadvantages, the pillared anionic clays may be prepared by different methods such as the exchange of inorganic/organic anions, and the structure reconstruction or direct coprecipitation. In any case, the design of pillared anionic clays is less common than cationic clays [19].

The future perspectives related to the use of anionic clays in the catalysis field are focused on the design of an efficient method to incorporate active metal anions in the interlayer spacing with high regioselectivity. Another parameter that can be developed is the controlled exfoliation of the sheets to obtain materials with high surface area. The incorporation of metal complexes or metal nanoparticles to form functionalized hydrotalcites and to carry out one-pot catalytic reactions is another important point to be addressed.

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