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Preparation and catalytic properties of cationic and anionic clays

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Abstract

The structure, main properties and preparation methods of cationic and anionic clays are reviewed in light of the versatility and potential of these materials. Recently reported catalytic applications in some fields of high industrial and scientific relevance (organic or fine chemistry, environmental catalysis, etc.) are also summarized. Clays exhibit many profitable features (such as low cost, wide range of preparation variables, use in catalytic amounts, ease of set-up and work-up, gain in yield and/or selectivity, etc.) which may be useful tools in the move towards establishing environmentally friendly technologies. Furthermore, the preparation and properties of pillared layer cationic or anionic clays are also discussed, considering that the upgrading of these materials by the pillaring process opens new and interesting perspectives, on account also of possible shape selective effects. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Clays; Hydrotalcites; Pillared clays; Solid acids; Solid bases; Heterogeneous catalysis; Environmental catalysis

1. Introduction

Clays are among the most common minerals on the earth's surface and have been used by man for centuries. As long as 25 000 years ago, primitive people in Europe and Asia used clays to produce figures, pottery and ceramics. Clays are very versatile materials and hundreds of millions of tons currently find applications in many different areas. In addition to ceramics, including building materials, clays also are used as paper coatings and fillings, drilling muds, foundry moulds, pharmaceuticals, cat litters, etc. Furthermore, clays can be used as adsorbents, catalysts or catalyst supports, ion exchangers, decolorizing agents, etc., depending on their specific properties. For example, the high surface area and surface polarity of some clays determine high adsorption and water-retention capacities. Clays also play an important role in agriculture, considering that many soils contain large amounts of clay materials, which determine key soil properties (structure, texture, water retention, fertility, etc.) [1,3].

Clays may be divided into two broad groups: cationic clays, widespread in nature, and anionic clays, rarer in nature but relatively simple and inexpensive to synthesize. The cationic clays have negatively charged alumino-silicate layers, which have cations in the interlayer space to balance the charge, while the anionic clays have positively charged metal hydroxide layers with balancing anions and water molecules located interstitially [4]. Cationic clays are generally prepared starting from the minerals, whereas anionic clays used industrially are synthetic [5–9].

The aim of this paper is to compare the chemistry and applications of cationic and anionic clays, focus-

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ing attention on various aspects, such as structure, composition, preparation and properties, as well as the role of these parameters in catalytic applications. The technological upgrading of these materials, i.e., the transition from two- to three-dimensional structures via the preparation of pillared clays, also is briefly examined, including a discussion of the main problems related to the synthesis of these materials and possible industrial applications.

2. Cationic clays

2.1. Structure and properties

Clay minerals are for the most part hydrous layer silicates of the phyllosilicate family (i.e. layer silicates or silicates based on a two-dimensional structure), in which the basic building blocks are the Si(O,OH) tetrahedra and the $\mathrm{M(O,OH)_6}$ octahedra (where $\mathrm{M{=}Al^{3+}}$, $\mathrm{Mg^{2+}}$, $\mathrm{Fe^{3+}}$ or $\mathrm{Fe^{2+}}$). The combination of a sheet of tetrahedra with a sheet of octahedra gives rise to the layer (thick 0.7 nm ca.) of the 1:1 minerals (kaolinites or serpentinites for $\mathrm{M{=}Al^{3+}}$ or $\mathrm{Mg^{2+}}$, respectively), while in the layer of the 2:1 type clays (thick 1.0 nm ca.) a sheet of octahedra is sandwiched between two sheets of Si-tetrahedra (Fig. 1(A)). Clay minerals can be dioctahedral or trioctahedral, based on the number of octahedral sites per unit cell occupied, which in turn depends essentially on the cation present (for example, $\mathrm{Al^{3+}}$ or $\mathrm{Mg^{2+}}$) in the octahedral sheets.

Table 1 reports the main, most industrially interesting 2:1 clays: the electroneutral structures present in nature are pyrophyllite (dioctahedral) and talc (trioctahedral), while the other minerals were obtained by isomorphous substitution during their formation in "dirty" geochemical environment of $\mathrm{Si^{4+}}$ in the tetrahedral sheet or $\mathrm{Al^{3+}}$ or $\mathrm{Mg^{2+}}$ in the octahedral sheet. When the incoming cation has a lower valence than the outgoing cation, the lattice becomes negatively charged and neutrality is maintained by the exchangeable cations. The following general formulas may be adopted for the dioctahedral and trioctahedral clays:

$$(\mathrm{Si}_{8-x}\mathrm{M}_x)^{\mathrm{T}}(\mathrm{Al}_{4-y}\mathrm{M}'_y)^{\mathrm{O}}(\mathrm{OH})_4\mathrm{O}_{20}\mathrm{M}''^{n+}{}_{(x+y)/n}m\mathrm{H_2O},$$

$$(\mathrm{Si}_{8-x}\mathrm{M}_x)^{\mathrm{T}}(\mathrm{Mg}_{6-y}\mathrm{M}'_y)^{\mathrm{O}}(\mathrm{OH})_4\mathrm{O}_{20}\mathrm{M}''^{n+}{}_{(x+y)/n}m\mathrm{H_2O},$$

where T and O refer to the tetrahedral and octahedral sheets, respectively, M and M′ have one unit of charge less than the substituted cation and M″ is the

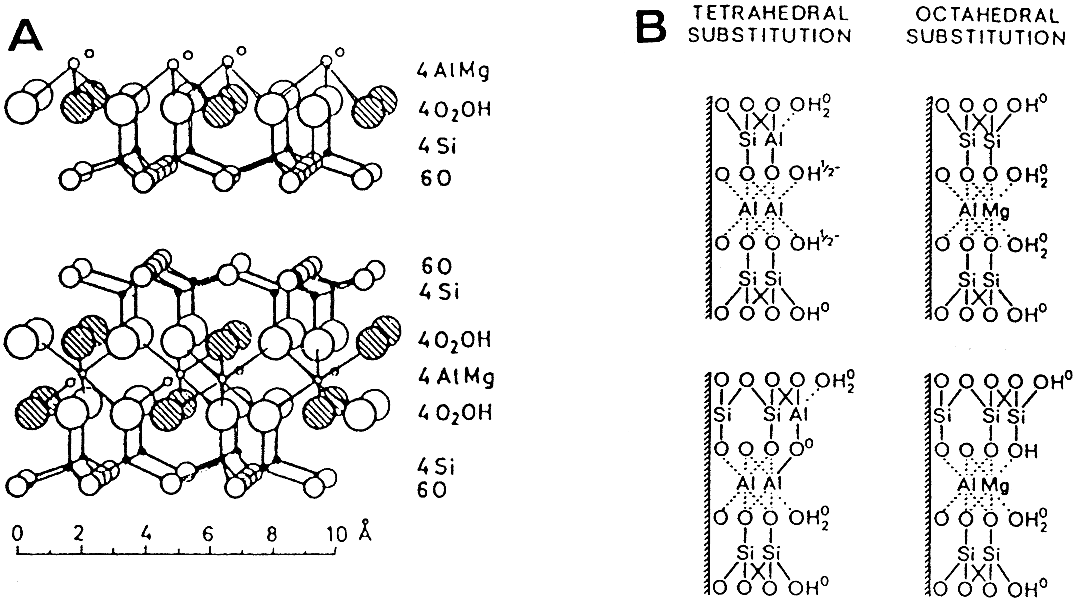

Fig. 1. Structure of a smectite (A) and effects (at pH=6.5) of tetrahedral and octahedral substitutions in the smectite layers on the edge charges (B) [1,15].

Table 1
Classification of the 2:1 clays [1,13]

Layer charge per unit cell	Group name	Octahedral occupancy	Species
0.0	Pyrophillite	Dioctahedral	Pyrophyllite
	Talc	Trioctahedral	Talc
0.5–1.2	Smectite	Dioctahedral	Montmorillonite, beidellite
		Trioctahedral	Hectorite, saponite
1.2–1.8	Vermiculite	Dioctahedral	Dioctahedral vermiculite
		Trioctahedral	Trioctahedral vermiculite
≅2.0	Mica	Dioctahedral	Muscovite, paragonite
		Trioctahedral	Phlogopite, biotite
≅4.0	Brittle mica	Dioctahedral	Margarite
		Trioctahedral	Clintonite
Variable	Chlorite	Dioctahedral	Donbassite
		Trioctahedral	Clinochlore

exchangeable cation with valence *n*; as a function of the degree of isomorphous substitution ($x+y$), some broad classes may be identified (Table 1). Isomorphous substitution most often occurs in the octahedral sheets, but also can occur in the tetrahedral sheets. In the smectite group both dioctahedral montmorillonite and trioctahedral hectorite have isomorphous substitution in the octahedral sheets (Mg^{2+} for part of the Al^{3+} in montmorillonite and Li^{+} for Mg^{2+} in hectorite). In contrast, for the smectites beidellite (dioctahedral) and saponite (trioctahedral), the negative charge on the layers is due to the isomorphous substitution of Al^{3+} for some of the Si^{4+} ions in the tetrahedral sheets. Finally, nontronites are minerals in the smectite group that contain Fe^{3+} instead of Al^{3+} in the octahedral sheets.

The properties of clays are affected considerably by their composition and particle size. For information beyond that summarized here, reference should be made to the original literature (e.g., [1–3,10–14]). For example, the XRD powder patterns of clays are composed of two sets of lines: 001 lines or basal reflections, that are sensitive to the state of the minerals (hydration, type of exchangeable cations, etc.), and the hk0+hkl reflections, which are typical of each mineral. The surface area determined by N_2 adsorption (50–150 m^2/g ca.) decreases with increasing the particle size, evidencing that only the "external" surface area is measured and N_2 does not penetrate into the interlamellar space between the individual clay layers. Furthermore, in all cases the experimental values are significantly lower than those calculated for single layer particles (for example, 800 m^2/g for 2 µm particles), mainly due to the fact that elementary layers are not present, but are stacked together into aggregates [1].

The different surface areas determined as a function of the drying procedure and, mainly, type of exchangeable cations, indicate that the number of layers per aggregate and the agglomeration of the aggregates in a powder are cation and drying procedure dependent. The total surface area (i.e. interlamellar surface area included) may be measured using polar probe molecules of known size, which penetrate the interlamellar space to form either monolayers or double sheets [14]. However, the packing density of these molecules depends on the charge density of the clays and, consequently, the surface area covered by one molecule varies from clay to clay.

Also related to the particle size are the cation exchange capacity (CEC) and the surface chemistry of clays. The structural formulae give the amount of negative charge per unit cell due to the isomorphous substitution (compensated by an equal number of positive charges of the exchangeable cations); this represents the pH-independent part of the CEC. Moreover, it must be considered that at the edges of the crystals the sheet structure is broken and terminated by OH-groups, that, as a function of pH, can adsorb protons becoming positively charged, or deprotonate, becoming negatively charged and contributing to the CEC (Fig. 1(B)). The contribution of the edge sites depends on the crystal size, type of exchangeable cations and pH. This contribution, for example, for particles of 100 nm may reach about 10% of the total CEC.

Determination of the layer charge density (defined as CEC per unit of surface) is obviously subject to the same problems, with a further difficulty related to the determination of the surface area previously discussed. Ion exchange with alkylammonium ions with varying chain length has been proposed to determine this parameter. This method, however, is not simple due to the variation in charge density from one particle to another and the difficulty of estimating the amount of chain protruding out of the clay sheet and, consequently, the relationship between charge density and particle size [16]. However, a charge density of 1 e$^-$/nm^2 ca. has been reported as average for smectites [17].

As a function of their small particles, clays present acid surfaces. Smectites, for example, exhibit both Brønsted and Lewis acid sites on the edges of the crystals. The Brønsted acid sites are the external OH-groups, while the Lewis sites are the exposed or three-coordinated Al^{3+} ions, substituting for the Si^{4+} ions in the tetrahedral sheets. The acid strength of the Brønsted sites may be determined by Hammet indicators in an aprotic solvent, butylammine titration or IR spectroscopy using probe molecules [14,18,19], with a direct correlation between acid strength and clay composition (Table 2). For the H$^+$-montmorillonite the number of acid sites titrated by butylammine is significantly smaller than the CEC (0.98 meq/g), showing that in an aprotic solvent the interlamellar space is not totally available for the reaction. Furthermore, the surface acidity decreases as the amount of residual water in the clay increases, with an extension related to the nature of the exchangeable cations (very significant for Ca^{2+} and Mg^{2+} ions or almost negligible for K$^+$ or Al^{3+} ions) [1].

Table 2
Acid strength and total acidity of different montmorillonites (in brackets, the total acidity values determined by means of butylamine) [14,22]

Smectite	H_0
Na$^+$-montmorillonite (0.04 meq/g)	$-3.0 < H_0 < +1.5$
NH_4^+-montmorillonite	$-3.0 < H_0 < +1.5$
H$^+$-montmorillonite (0.65 meq/g)	$-8.2 < H_0 < 5.6$
Acid activated clay	< -8.2

Not only acid sites, but also electron-accepting or oxidizing sites may be located at the edges or in the structure. The former may be identified as trigonal Al^{3+} ions, acting as Lewis sites, while Fe^{3+} ions in the lattice are the structural oxidizing sites [11]. Moreover, redox properties may also be induced by the exchangeable cations, such as Cu^{2+}, Ag$^+$, Fe^{3+} and Ru^{3+} [20,21]. However, it must be pointed out that only the acid or oxidizing sites are not important in catalysis. Indeed a solid surface may interact with organic molecules also as a function of its hydrophobicity. A weak interaction precludes any catalytic step, while too strong clinging of organic products to the mineral surface makes desorption too slow or impossible. Again, the hydrophilic–hydrophobic character of the surface may be manipulated by an appropriate choice of the exchangeable cations [19].

Due to its industrial and economic importance, the clay–water system has been thoroughly investigated. In liquid water many clays swell, i.e. the distance between the elementary layers increases so much that the aggregates disintegrate, with transformation of the original suspension into a gel, which is not thermodynamically stable, but tends with time to coagulate or flocculate (aging process). This process is slow, due to the simultaneous effects of two opposite forces: electrical double layer repulsion and the London–Van der Waals attraction. However, it must be pointed out that recent measurements indicated that single clay sheets do not exist in appreciable amounts in aqueous suspension [23]. The clay particles in suspension seem to be the same as in the air-dry powder, with a change only in the distances between the elementary layers in the aggregates, due to the water adsorption. In other words, the clay particles swell, but do not disintegrate "remembering" the original situation.

2.2. *Synthesis and catalytic applications*

Cationic clays are mainly obtained from natural materials, that invariably contain impurities such as quartz, calcite, feldspars, etc., although, they may also be synthesized, such as for example laponite® (analog of hectorite, by Laporte Industries). By means of centrifugation it is possible to obtain a <2 μm suspension of clay, while the precipitate mainly contains the impurities. Amorphous Fe- or Al-oxides however may remain adsorbed on the clay particles and chemical treatments to remove them, for example using dithionate, are not simple and present many problems [24].

Most usual is the acid treatment of clays, in particular montmorillonites, which may be performed either by simple washing with a mineral acid (i.e. exchanging the interlamellar cations with protons) [25] or by heating for variable times a 1% ca. suspension of clay in mineral acid (for example at 368 K with 30% H_2SO_4) [26,27]. In this way, it is possible to obtain a surface acidity (Table 2) ranging between those of nitric and concentrated sulfuric acid. Acid treatment produces a clay in which all the original exchangeable cations have been replaced by protons; however, this clay is unstable and converts to clay containing exchangeable ions exsolved from the lattice [28]. It must be pointed out that optimum acid treatment conditions vary from one clay to another, as a function of the chemical composition, level of hydration and, mainly, of the nature of the exchangeable cations. However, a commercial modified montmorillonite (K10, by Sud-Chemie or Fluka), used industrially as catalyst in hydrocarbon cracking and, thus, a well-defined and reliable material may be employed as a reference material.

Clays or acid treated clays may also be effective supports for many inorganic salt catalysts, including the Lewis acid $ZnCl_2$ and ferric or copper nitrates [19,25,29–31]. "Clayzic", "Kaozic" or "Japzic" are acronyms for K10-, kaolinite- or Japanese acid clay-supported zinc chloride, respectively. They can be prepared by dissolving at 333 K, 10 g of $ZnCl_2$ in 100 ml of acetonitrile and, under energetic stirring, adding 20 g of clay in small portions. Stirring is maintained for 30 min and then the solvent is removed under reduced pressure, heating on a water bath for 30 min at 323 K and then at 368 K for another 30 min. The resulting powder is powdered in a mortar, dried overnight under vacuum in an oven at 453 K and kept at 533 K under air at atmospheric pressure. However, different drying or storing procedures have been reported.

Analogously, "Clayfen" and "Claycop" are the acronyms for iron(III) or copper(II) nitrate supported on K10 clay [30], prepared in a similar way. For example, 22.5 g of iron(III) nitrate nonahydrate is added to 375 ml of acetone, stirring vigorously until complete dissolution. Successively, 30 g of K10 clay are added in small amounts under energetic stirring and stirring is continued for another 5 min. The solvent is then removed under reduced pressure, using a rotatory evaporator on a water bath at 323 K. After 30 min, the dry solid crust adhering to the flask walls is flaked off and crushed with a spatula, and rotatory evaporator drying is resumed for another 30 min (yield 50 g ca.).

The first industrial application of clays as catalysts date back to the year 1915, while acid treated smectites have been known for more than 50 years as catalysts for oil cracking (Houdry process) although after 1964 they were replaced by zeolites, due to the better zeolite activity and selectivity [3,32]. However, solid acid catalysts, in particular acid treated montmorillonites, can be used to catalyze a wide range of important industrial processes such as isomerization, liquid refining and Friedel–Crafts alkylation, playing an increasing role in the move towards establishing environmentally friendly technologies.

The acid treatment conditions corresponding to maximum catalytic activity depend on the precise reaction being catalyzed [26]. Reactions between polar molecules require clays acid treated in mild conditions or for short times, capitalizing on the large number of acid sites available in the internal surface. In contrast, the surface accessible to non-polar molecules consists only of the external face and edge areas of the clay platelets. These reactions require more severely acid treated clays and the catalytic activity depends on fine tuning of the changes in surface area and decrease in cation exchange capacity. However, in a swelling medium, optimum catalytic activity may be achieved not through acid treatment, but simply by ion exchange with acidic cations such as Al^{3+} ions; on the contrary, this last treatment has a negligible effect in a non-swelling medium [29].

Also for supported $ZnCl_2$ Lewis acid catalysts the activity depends on the nature of the organic substrate. Maximum activity in the Friedel–Crafts alkylation of benzene by benzyl chloride, for example, was found using acid treated clays for which the acid treatment lasted for a very long time (20 h). This support exhibited almost no clay character, relatively low surface area and formation of mesopores (10–14 nm range); active $ZnCl_2$ appears to be that adsorbed in these mesopores [29]. On the contrary, using anisole instead of benzene, optimum activity was achieved with supports subjected to shorter treatments, with evidence of a significant contribution by the Brønsted acid sites on the clays. This result together with the lower than expected activity of the catalyst, suggests that the $ZnCl_2$ Lewis acid sites are quite strongly coordinated by anisole, significantly reducing their catalytic activity [29]. It is worth noting that a recent note reported a quantitative yield for this reaction, after 15 min at room temperature, using the K10 clay impregnated with zinc chloride (Clayzic) [33].

Also Friedel–Crafts acylations may be effectively catalyzed by clays modified through exchange of the interlamellar cations or impregnation of metal chlorides [31]. A comparison of the catalytic performances in the benzoylation of mesitylene (Table 3) and anisole showed the superior performances of the exchanged clays in comparison to those of the impregnated clays. Moreover, in the impregnated clays, the catalytic activity depends more on the activation procedure adopted than the nature of the starting clay. Furthermore, the authors reported for the exchanged clays a strong dependence on the type of reaction and nature of the reaction partners, with, for example, an efficiency scale in the acylation of *p*-xylene by benzoyl chloride for the different cations ($Zr^{4+}<Ti^{4+}<Al^{3+}<Cu^{2+}<Cr^{3+}<Co^{2+}<Zn^{2+}<Fe^{3+}$) totally different from the normal sequence of bulk metallic chlorides in Friedel–Crafts reactions [34,35].

The applications of modified-clay catalysts are not limited to the acid-catalyzed reactions, but many other interesting examples have been reported in the literature [19,25,29,30], although nowadays only on a laboratory scale. For example, we may report the nitration of phenols, that normally is performed using mixtures of nitric and sulfuric acids, with only modest overall yields (60% ca.) and formation, together with the normal ortho- and para-substituted derivatives, of the meta isomer and by-products of polynitration [36]. The clay-supported ferric nitrate (Clayfen) not only improves significantly the overall yield in the nitration of phenol (up to 90% ca.), but is also very active in the nitration of many other phenols (Table 4), with a high selectivity in ortho, para mononitration [25]. It should be noted that for the estron nitration (an important process in the pharmaceutical industry as the gateway to various estrogenic drugs) the yield obtained is a significant improvement over the best value previously reported (39%) [37], decreasing the cost per gram of product by a factor of 6 [38].

Table 3
Benzoylation of mesitylene (5 ml) by benzoyl chloride (1.4 g) in the presence of impregnated or exchanged catalysts [31]

Catalyst	Reaction temperature (K)	Reaction time (min)	Yield (%)
Kaozic-533[a]	343	1800	85
Japzic-533	343	1800	72
Kaozic-533	433	60	74
Japzic-533	433	60	100
Japzic-673	433	15	100
Clayzic-533	433	10	100
K10-Al^{3+}	433	15	98
K10-Ti^{4+}	433	15	100
K10-Cr^{3+}	433	15	94
K10-Fe^{3+}	433	15	98
K10-Co^{2+}	433	15	100
K10-Cu^{2+}	433	15	84
K10-Zn^{2+}	433	15	85

[a] Activation temperature (K).

Table 4
Nitration of various phenols using clay-supported ferric nitrate (Clayfen) [25]

Phenol	Ortho (%)	Para (%)	Conditions
—	39	41	Ether, 20 h
4-CH_3	58	—	Ether, 20 h
3-CH_3	20	34	Ether, 20 h
4-Cl	88	—	Ether, 20 h
4-F	69	—	Toluene, 5 h
β-Naphthol	63	—	Tetrahydrofuran, 2 h
4-*t*-C_4H_9	92	—	Toluene, 1.5 h
3-OH	58	—	Ether, 2 h
4-CHO	93	—	Toluene, 72 h
Estrone	55	—	Toluene, 24 h

In concluding this section, it must be underlined that the use in many organic syntheses of clay or clay-modified catalysts commends itself by its simple implementation, the small amount of catalyst required (in comparison to standard Lewis acids, such as $AlCl_3$) and the use of most environmentally compatible conditions and/or substances, for instance ferric or other metal chlorides trapped between the layers of a commercial and inexpensive clay.

3. Anionic clays

3.1. *Structure and properties*

Anionic clays are natural or synthetic lamellar mixed hydroxides with interlayer spaces containing

Table 5
Composition, crystallographic parameters and symmetry for some natural anionic clays [39]

Mineral	Chemical composition	Unit cell parameters		Symmetry
		a (nm)	*c* (nm)	
Hydrotalcite	$Mg_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$	0.3054	2.281	3R
Manasseite	$Mg_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$	0.310	1.56	2H
Pyroaurite	$Mg_6Fe_2(OH)_{16}CO_3 \cdot 4H_2O$	0.3109	2.341	3R
Sjøgrenite	$Mg_6Fe_2(OH)_{16}CO_3 \cdot 4H_2O$	0.3113	1.561	2H
Stichtite	$Mg_6Cr_2(OH)_{16}CO_3 \cdot 4H_2O$	0.310	2.34	3R
Barbertonite	$Mg_6Cr_2(OH)_{16}CO_3 \cdot 4H_2O$	0.310	1.56	2H
Takovite	$Ni_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$	0.3025	2.259	3R
Reevesite	$Ni_6Fe_2(OH)_{16}CO_3 \cdot 4H_2O$	0.3081	2.305	3R
Meixnerite	$Mg_6Al_2(OH)_{16}(OH)_2 \cdot 4H_2O$	0.3046	2.292	3R
Coalingite	$Mg_{10}Fe_2(OH)_{24}CO_3 \cdot 2H_2O$	0.312	3.75	3R

exchangeable anions; many names are used as a function of the composition and polytype form of the minerals (Table 5). Furthermore, the general terms hydrotalcite-type (HT) compounds or layered double hydroxides (LDH's) are also widely used. The former is probably due to the fact that extensive characterizations have been carried out on hydrotalcite (a Mg/Al hydroxycarbonate), rather than on other similar compounds, and that it is easy and inexpensive to synthesize. On the other hand, the reference name LDH's is derived from early works of Feithnecht, who called these compounds "Doppelschichtstrukturen" (double sheet structures), hypothesizing a structure with intercalated hydroxide layers [40,41]. This hypothesis was refuted many years later on the basis of single crystal XRD analysis [42,43], which showed that all the cations are localized in the same layer, with the anions and water molecules located in the interlayer region. However, it must be pointed out that the terms HT compounds or anionic clays also are not generally accepted, taking into account that in the first case the term refers strictly to a specific mineral and that these compounds do not fulfill some clay requirements, for example the very small particle size [1–3,44].

Anionic clays may be defined by their chemical composition, basal spacing and stacking sequence. The general formula to describe the chemical composition is:

$$[M^{z+}_{1-x}M^{3+}_{x}(OH)_2]^{b+}[A^{n-}_{b/n}]mH_2O,$$

where M=metal, A=interlayer anion, and b=x or $2x-1$ for z=2 or 1, respectively. Anionic clays have structures similar to that of brucite $Mg(OH)_2$, and crystallize in a layer-type lattice as a consequence of the presence of relatively small twofold positively charged cations in close proximity to the non-spherosymmetrical and highly polarizable OH^- ions [45]. Each Mg^{2+} ion is octahedrally surrounded by six OH^- ions and the different octahedra share edges to form infinite sheets [6–9,45]. The sheets are stacked one on top of the other and are held together by weak interactions through hydrogen [9,45]. If some Mg^{2+} ions are replaced isomorphously by cations with higher charge, but similar radius [46], the brucite-type sheets become positively charged and the electrical neutrality is maintained by anions located in disordered interlayer domains containing water molecules (Fig. 2).

The OH-sheets may exhibit two stacking sequences, rhombohedral and hexagonal [47]. The two forms can be distinguished only by XRD analysis, since they have the same physical properties as the mixed oxides obtained by their thermal decomposition. Hydrotalcite crystallizes with a rhombohedral 3R stacking sequence, the parameter of the unit cell being a and $c=3c'$ (where c' is the thickness of one layer consisting of a brucite-like sheet and one interlayer), while the polytype form, manasseite, crystallizes with a hexagonal 2H stacking sequence, the parameter of the unit cell being a and $c=2c$ (Table 5). However, the form normally obtained by synthesis is the three-layer polytype (i.e. rhombohedral), while the two-layer polytype (i.e. hexagonal) can be the form which is obtained at high temperatures [48].

The structures of anionic clays may accommodate a wide range of variables (nature and ratio of the cations, type of charge balancing anions, amount of

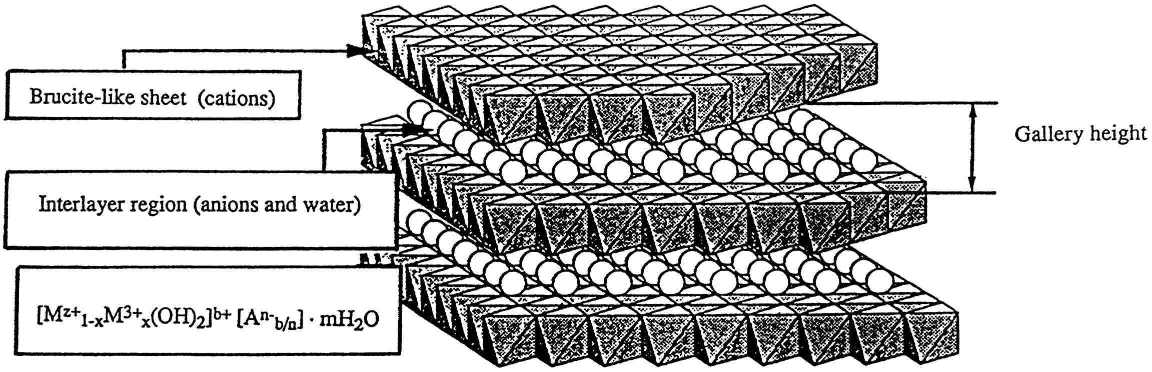

Fig. 2. Schematic representation of the hydrotalcite-type anionic clay structure [44].

Table 6
Factors influencing the synthesis of anionic clays [7,8]

Structural variables	Preparation variables
Cation size	pH
x value	Precipitation method
Cation stereochemistry	Reagent concentration
Cation mixture	Temperature and aging
Nature of the anion	Washing and drying
	Presence of impurities

interlayer water, crystal morphology and size). Only a few of these variations appear in nature however and for instance, carbonate is the anion preferred [4,7,9,39]. On the contrary, a very high number of variables have been reported for synthetic clays (Table 6), which make it possible to produce tailor-made materials able to fulfill specific requirements. For example, even anionic clays containing Li^+ ions or the highly instable V^{3+} ions have been reported in the literature [49,50], as well as a very wide range of possible anions: inorganic and organic anions, iso and heteropolyanions, complex anions and metallorganic complexes [7,9,44]. There is practically no limitation to the nature of the anions, which only have not to form strong complexes with the cation present. The only problems may be the preparation of compounds with anions different from carbonates, due to the difficulty of avoiding any contamination from CO_2 [51] and the instability of the anions in the pH range in which the synthesis of the relative HT compounds occurs, such as may occur with the Keggin-like heteropolyanions [52].

All divalent or trivalent cations having an ionic radius similar to that of Mg^{2+} ions [46] may be accommodated in the octahedral sites in the brucite-type sheets and form anionic clays. However, even though Cu^{2+} ions have a suitable ionic radius, they give rise preferentially to the precipitation of malachite-like phases, because of the Jahn–Teller effect, which for d^9 ions favors the formation of distorted octahedral structures [53]. Other cations (e.g. Mg^{2+}, Co^{2+} or Zn^{2+}), which can form regular octahedral structures [53], favor the entrance of Cu^{2+} ions into ternary phases, which are obtained without side phases for Cu^{2+}/M^{2+} ratios near to 1 [54,55].

Furthermore, notwithstanding the claims that HT compounds form for x values in the general formula in the range 0.1–0.5, there are many indications that pure phases may form only for a narrow range ($0.20<x<0.34$). For instance, Brindley and Kikkawa [56] reported for the Mg/Al system that for higher values, the increased number of neighboring Al-containing octahedra leads to the formation of $Al(OH)_3$ and, analogously low x values lead to a high density of Mg-containing octahedra in the brucite-type sheets with segregation of $Mg(OH)_2$. However, in many cases the side phases are amorphous, therefore not detectable by XRD, but only by other techniques such as thermogravimetric, electron microscopy or solid state ^{27}Al MASNMR analyses [9].

Water molecules and anions are located in the interlayer space, and structural and physical properties evidence the strongly disordered nature of these regions, for which a quasi-liquid state has been claimed [42,44]. The water content depends on the temperature, water vapor pressure and nature of the anions present. For example, anionic clays containing nitrates or carbonates may lose about one third of their interlayer water at low temperatures (<373 K) [57]. Furthermore, in microcrystalline solids a large amount of water may be adsorbed on the surface of the crystallites, with a partial overlapping of the dehydration and dehydroxylation reactions [44]. It is worth noting that the maximum amount of interlayer water also may be calculated on the basis of sites present in the close packed configuration of oxygen atoms, subtracting the sites occupied by the anions [7,9].

As previously reported, normally anionic clays exhibit particle sizes higher than those claimed for clay minerals and this reflects on the surface area values, that for the dried precipitates are generally lower than 100 m^2/g. Analogously to that previously shown for smectites, it is evident that these values refer only to the "external" area, and this may be even better understood considering the higher charge density of anionic clays (4 instead of 1 e^-/nm^2) [17]. This high charge density creates strong electrostatic forces between the brucite-type sheets and the anions, thus swelling is much more difficult and has been reported only using, for instance, glycerol to produce HT compounds containing long-chain organic acids from meixnerite [58,59].

Because of their particular structure, anionic clays have good anion exchange capacities. Although the true exchange capacity (1.0–1.5 meq/g [4]) is usually much less than the theoretical one (3.3 meq/g for hydrotalcite [60,61]), they show a resistance towards temperature higher than that of anion exchange resins and thus are used in some high temperature applications, such as treatment of the cooling water of nuclear reactors [62]. The selectivity in the exchange increases with increasing anion charge density [51,63], i.e. anionic clays strongly prefer multiply charged anions and compounds containing nitrates or chlorides have to be indicated as the best precursors for exchange reactions. However, very important is the pH of the solution, which may favor or prevent the exchange [60] and has to be compatible with both the range of stability of the starting anionic clay and the anion.

Finally, it must be noted that the interlayer space can be used to increase the total amount of metals, which may be introduced in anionic form (chromates, ferro or ferricyanides, etc.), or to introduce cations which are not compatible with the octahedral sites of the brucite-type sheets (for example Mo^{4+} or Ir^{4+}), thus preparing new materials with unusual properties [64].

Anionic clays exhibit poor basic properties, sensibly lower than those of the mixed oxides obtained by their thermal decomposition [7,9,65]. It is hypothesized that adsorbed water inhibits access to the basic sites on the surface; however, the strength and nature of basic sites in dried anionic clays has not been fully clarified [66]. Moreover, basic properties depend also on composition, for example Zn/Al, Zn/Cr or Ni/Al anionic clays are less basic than Mg/Al clay [9,17].

The thermal decomposition of anionic clays is interesting and important, giving rise to mixed oxides of industrial interest for catalytic or other practical applications [7,8], and is generally characterized by two endothermic transitions. The first transition (370–570 K) corresponds to the loss of interlayer water, while the second takes places at higher temperatures and is due to the loss of hydroxyl groups from the brucite-type sheets and of the anions [7,9]. These transitions depend qualitatively and quantitatively on many factors such as nature and relative amounts of cations, type of anions, crystallinity, and heating atmosphere (for variable valence cations such as Co^{2+}, Fe^{2+}, Cr^{3+}, Mn^{3+}, etc.). For example, the temperature of anion elimination may range from the 473 K of bromates [67] to the 1200–1240 K of sulfates [68]. In addition, heating anionic clays in air or nitrogen results in the formation of stoichiometric spinels and free divalent oxides. The spinel formation depends considerably on the nature of the cations; for example $NiCr_2O_4$ forms at a lower temperature than $NiAl_2O_4$ (873 K instead of 1173 K), with little influence of the heating atmosphere [69].

Therefore, there is a very interesting range between the decomposition temperature of an anionic clay and that of spinel formation (characterized by an XRD pattern corresponding to that of ICDD), in which metastable, generally poorly crystallized phases form. These phases have been referred to in the literature with many different names (NaCl-type mixed oxides, spinel-type phases or simply mixed oxides or mixed oxide solutions), however all authors agree that these mixed oxides have disordered structures, containing an excess of divalent cations in comparison to the amount present in stoichiometric spinels [7,9,70].

SEM analysis of these phases showed a retention of the original morphology, suggesting that during thermal decomposition steam and carbon dioxide escape through holes in the surface, without extensive change in the crystal morphology or dealumination of the brucite-type sheets [71,72]. In agreement with this mechanism, initially the surface area increases considerably (2–3 times), then a further increase in temperature and formation of the stoichiometric spinel give rise to a dramatic decrease in the surface area [9]. The most interesting properties of these mixed oxides may be summarized as follows [7,8]:

(A) *High surface area* (100–300 m^2/g).

(B) *Homogeneous interdispersion* of the elements thermally stable also in reducing conditions, with formation of very small and stable metal crystallites. Impregnation procedures for the preparation of metal catalysts normally cannot achieve such high metal dispersion [6].

(C) *Synergetic effects* between the elements, due to the intimate interdispersion, which favors, for example, the development of unusual basic or hydrogenating properties. It is worth noting that basic properties depend significantly on composition and calcination temperature (Fig. 3).

(D) *Memory effect* [42], which allows reconstruction under mild conditions of the original structure by contact with solutions containing various anions.

3.2. Synthesis and catalytic applications

Synthetic anionic clays, as such or, mainly, after thermal decomposition, find many industrial applications and probably more will be found in the future in totally unexpected areas (Fig. 4). Furthermore, although the available literature on anionic clays is significantly less than that for cationic clays, anionic clays are the most promising precursors of multicomponent catalysts for many catalytic reactions of industrial interest, complementary to those of cationic clays.

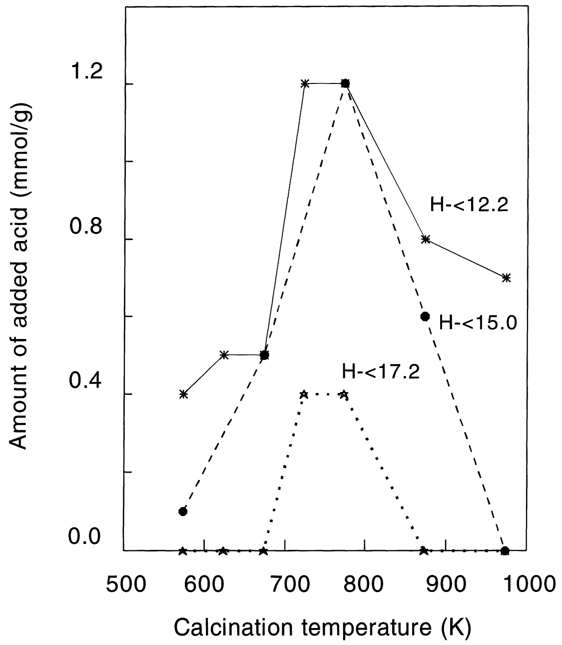

Fig. 3. Strength of the basic sites as a function of the calcination temperature for Mg/Al anionic clays [65].

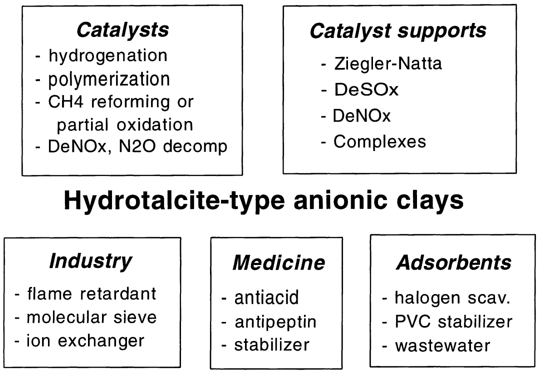

Fig. 4. Main industrial applications of anionic clays (as such or after thermal decomposition) [7,8].

Anionic clays may be synthesized by various techniques. This does not mean that it is easy to prepare pure compounds, but only that different methods may be adopted as a function of the composition required. Considering the different methods of preparation (precipitation at constant pH (also called coprecipitation to indicate that all cations precipitate simultaneously, in a ratio fixed by the starting solutions), precipitation at variable pH, deposition/precipitation reactions, hydrothermal synthesis, anion exchange, structure reconstruction, electrochemical methods, hydrolysis reaction) [7,9,44], it is evident that coprecipitation is the most useful method to prepare large amounts of anionic clays. However, in some cases true coprecipitation conditions may not be required, taking into account that: (i) the presence in a mixture smooths the differences in the precipitation pH of the single cations; (ii) aging and/or hydrothermal treatments may rectify improper precipitation conditions through dissolution/coprecipitation reactions; (iii) in some cases pure anionic clays may not be required or the presence of other species may have beneficial effects [73].

Together with the structural factors, other parameters have been claimed as important in the precipitation of anionic clays (Table 6). However, some of them are of limited importance, for example unlike that reported in the literature [44,74,75] in our preparations we have not observed any effect of the temperature and no aging procedure was necessary. In contrast, heating Cu-containing precipitates as slurry caused partial destruction of the HT structure with formation of malachite-type phases [54]. On the contrary, very important is the pH at which the precipitation occurs as well as the method of pH variation, which may modify both the nature and properties of the solids obtained [7,72]. On the basis of the values of precipitation pH of the single hydroxides [7,44,76], a pH range of 8–10 may be generally indicated as optimum to prepare most anionic clays.

High pH values give rise to the dissolution of aluminum and some other ions, and also phase segregation may be favored, as with Cu^{2+} ions forming CuO [77]. On the other hand at low pH the synthesis proceeds by a more complex pathway and is not complete, as indicated by the differences between the chemical composition of the phases obtained and that of the starting solutions [44]. Furthermore, the precipitation pH determines the crystallinity of the Cr-containing precipitates [44], probably because of the tendency of Cr^{3+} ions to form oligomer complexes.

Coprecipitation may be carried out at low or high supersaturation; the former is the method most frequently used and requires controlled experimental devices [78]. The conditions most commonly used are as follows: pH 7–10, temperature 333–353 K, low concentrations of the reagents and low flow of the streams. Washing is carried out with warm water and drying is performed at temperatures lower than 393 K. Anionic clays with anions other than carbonate may be prepared by precipitation under nitrogen using alkali hydroxides; however, small amounts of carbonates are always present [79].

Coprecipitation at high supersaturation gives rise to less crystalline materials, owing to the high number of crystallization nuclei. The precipitation may be carried out using the same devices reported above, by increasing the concentrations of the solutions and/or the addition rate, or by putting a solution of the salts of the elements into a solution containing a small excess of alkali bicarbonates or bicarbonate/carbonate mixtures, previously heated at 333 K [54,80]. This method is very simple and does not require a specific experimental apparatus. The only requirement is prolonged washing to reduce the amount of residual alkali because of the low solubility of the alkali bicarbonates. Examples of preparations carried out at different supersaturation conditions or using other methods have been reported in previous papers [7,9].

Many multicomponent catalysts have anionic clay precursors. Catalytic applications of the mixed oxides obtained by their controlled calcination include polymerization of alkene oxides, aldol condensation of aldehydes and ketones, methane or hydrocarbon steam reforming, methanation, methanol synthesis, higher-alcohols or hydrocarbon (Fischer–Tropsch) synthesis, etc. [7,8]. Over the past few years there has been an exponential increase in the references relative to these applications, most of them of industrial interest. Furthermore, new applications or upgrading are continuously being reported, concerning both compositions and reactions.

In regard to the new compositions, mention should be made of the recently reported synthesis of anionic clays containing noble metals, such as ruthenium, palladium or rhodium [81–84] or exhibiting a sheet-like morphology, with sheet broadness to thickness ratios ranging from 100 to 2000 [85]. New reactions worth mentioning here include the synthesis of aromatic compounds from alkanes [81], the selective hydrogenation of maleic anhydride to γ-butyrolactone (to produce new chlorine-free solvents) [86,87], the decomposition of N_2O [82], the partial oxidation of methane to synthesis gas [83,84,88] and the selective catalytic reduction (SCR) of NO by ammonia (Fig. 5) (as a possible inexpensive alternative to Cu-zeolites, mainly Cu-ZSM-5) [89].

Moreover, also for widely studied subjects, space is again available and new and interesting results have also been recently reported, such as for example those on the phases responsible for the high thermal stability

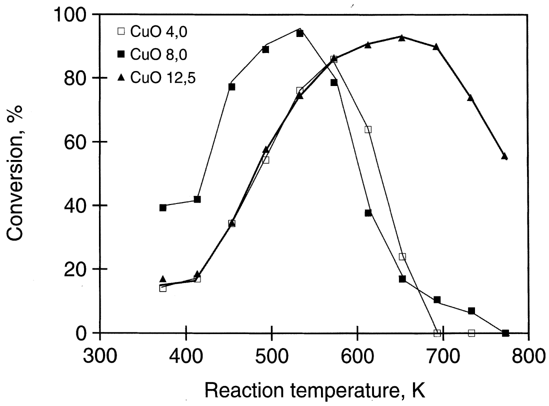

Fig. 5. Selective catalytic reduction of NO with NH_3 and O_2 using mixed oxides having different Cu-content (as CuO wt%), obtained by calcination for 14 h at 923 K of Cu/Mg/Al hydrotalcite-type anionic clays. Experimental conditions: NO=6000 ppm; NH_3/NO=1.25; O_2=3.0%; GHSV=10 000 h^{-1} [89].

of Ni/Al and Ni/Mg/Al catalysts [69,90,91] or those referring to the stereospecific polymerization of propylene oxide on Mg/Al mixed oxides, with formation of a crystalline, isotactic polymer fraction [92]. Referring to the applications of basic Mg/Al catalysts obtained by calcination of anionic clays, of particular importance is the possibility to substitute bases such as ammonia, ammonium salts or amines, for use in developing environmentally friendly solid catalysts that can be easily separated and recycled. Promising and charming applications have been recently reported in the field of fine chemicals or intermediates, regarding the production of citronitril (perfume as well as detergent and soap industry) [93], chalcones and flavonoids (pharmaceutical industry) [94] and alkylated phenols (octane boosters and organic intermediates) [95].

The textural and surface properties of these catalysts have been thoroughly investigated, and the possibility of modulating the activity as a function of the base strength needed for each reaction by an appropriate selection of the preparation conditions, Mg/Al ratio and calcination temperature has been shown [96–100]. For example, with increasing Mg/Al ratio, the total amount of basic sites increases; however, this is mainly due to the sites with $9.0 \leq pK \leq 13.3$, whereas the number of basic sites within $13.3 \leq pK \leq 16.5$ decreases (required, for example, in the condensation of benzaldehyde with ethyl bromoacetate) [96,98,100].

Finally, it must be pointed out that anionic clays may also be useful precursors of supports of Ziegler–Natta catalysts for ethylene polymerization or $DESO_x$ additives to FCC catalysts [7,101,102], showing high stability also in severe reaction conditions, excellent catalytic properties as well as catalyst regeneration. Furthermore, they also have been successfully used as supports of transition metal oxides for SCR of NO by NH_3, possible alternatives to less stable supports such as active carbons [103]. Therefore, in concluding this section, we have to emphasize the high flexibility and power of anionic clays as precursors of multicomponent catalysts. A broad spectrum of applications exists, and even more will probably be found in the future in totally unexpected areas, due to the possibilities of designing catalysts tailored for specific reactions and/or substrates.

4. Pillared clays

This section deals with materials having three-dimensional network structures. Whereas the materials discussed in the previous sections were two-dimensional layer structures (clays), the materials under discussion here have three-dimensional network structures like that of zeolites. Indeed, the main goal of the pillaring process has been and continues to be that of producing new and inexpensive materials, with properties complementary to those of zeolites (pore size and shape, acidity, redox properties, etc.).

Pillar means literally column for supporting part of a structure. Pillared clays (PILC's), then, are nanocomposite materials with open and rigid structures obtained by linking robust, three-dimensional species to a layered host. The term cross-linked clay (CLC) also has been used to distinguish PILC's in which chemical bonds have formed between the prop and the surface oxygens of the clay [1]. PILC's are typical examples of tailored materials, since it is possible to modify the structure and/or composition of either host or guest species. They can be shaped as powders, pellets, supported or self-standing film, or dispersed in solid or liquid matrices. Therefore, control of the pillaring process is a very promising means to obtain solids with (i) very high surface area (up to 600 m^2/g);

(ii) a broad spectrum of properties (structural, chemical, catalytic, ionic, etc.); and (iii) controlled internal structures, with reactive sites and/or species chosen to match particular applications or provide host structures for chemical or physical processes.

On the basis of the above data it is evident that PILC's are a so wide and important subject to require at least a single chapter. However, in order to complete our travel in clay chemistry and applications, the main aspects will be briefly summarized, with attention focused on the factors that may be designed to prepare particular materials. Moreover, more detailed and/or specific information on PILC's, may be obtained for example by consulting the literature for cationic clays (e.g., [1,3,104–111]) and anionic clays [9].

4.1. *Pillared cationic clays*

The pillaring process may be performed using a clay with a relatively low negative charge density and a chemical substance with a large positive charge. However, to create microporosity which is complementary to that of zeolites, a size of at least 0.7 nm is necessary [1]. Under the conditions that (i) the guest species are homogeneously distributed, (ii) the clay sheets are rigid and do not bend, (iii) all the sheets are pillared, and (iv) the adsorption of the pillaring molecules on the external surface is negligible, a two-dimensional channel system is generated (unlike in zeolites in which three-dimensional channel systems are present) (Fig. 6(A)). The final properties of PILC's can be modulated by carefully choosing the different parameters, such as nature of the pillaring agent, type of clay, pillaring procedure, thermal treatments, etc., thus offering a very powerful and flexible way to design new catalysts.

Many different pillaring species have been reported in the literature: organic compounds (alkylammonium and bicyclic amine cations), metal trischelates, organometallic complexes, metal cluster cations, metal oxide sols and polyoxocations. Many of these pillaring species have some drawbacks, such as low reactivity or lack of thermal stability. Polyoxocations are by far the most applied pillaring agent [1]. Many different polyoxocations (Al, Ni, Zr, Fe, Cr, Mg, Si, Bi, Be, B, Nb, Ta, Mo, Ti and more recently Cu and Ga) have been reported in the open and patent literature and clays with multimetallic pillars also have been prepared [1,3,109–114]. However, only for the Al-polyoxocation are the chemical composition, structure and charge well defined, in which the Keggin ion $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ is identified (Fig. 6(B)).

The structure of this ion has been defined by ^{27}Al NMR [115] and consists of a central Al^{3+}, tetrahedrally coordinated to four oxygens, each of which oxygens is connected to three edge-sharing Al-octahedra, $AlO(OH)_4(H_2O)$. However, the Al_{13} cations are partially hydrolyzed by the hydration water of the clay, and therefore a charge value of about 4^+ has been statistically assumed for the pillars, with an increase in the pillar density in the clay [1,3,110]. On the other hand, starting from any single clay, controlled calcination can be used to prepare a series of samples with cation exchange capacity ranging from that of the raw material down to virtually zero [110,116].

Preparation of pillared cationic clays consists in a controlled hydrolysis reaction which may be carried out in solution or in the interlamellar space of the clay

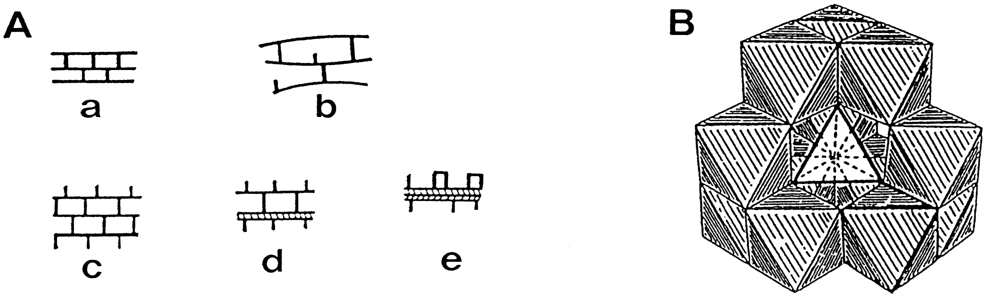

Fig. 6. Schematic representation of the: (A) possible PILC's [1]: (a) ideal, (b) with bent sheets, (c) with pillars on the external surface, (d) incompletely pillared, (e) unpillared, with micropores created by the external pillars; (B) $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ Keggin ion [1].

(the former allows better control of the nature of the polycations). When the hydrolysis reaction is carried out in solution, different methods may be employed: (i) addition of carbonates (Na, Mg, Zn, etc.) to a solution of $AlCl_3$; (ii) addition of alkali hydroxides (widely employed); (iii) dissolution of metallic aluminum in HCl and/or $AlCl_3$ (this is the method used to produce the commercial Chlorydrol, Rehei Chemical); and (iv) electrolysis of a 1 M solution of $AlCl_3$ [1,3]. The amount of Al_{13} species depends not only on the preparation method, but also on other factors, such as the nature of the reactants and their initial concentration, the degree of hydrolysis (i.e. the OH/Al ratio), the reaction temperature, the rate of addition of the reactants, and the aging conditions of the hydrolyzed solutions. For example, OH/Al ratios ranging from 2.0 to 2.2 have been reported as optimum in the literature [117].

Various other factors, such as the nature of the clay, may affect the pillaring reaction. For example, when highly charged vermiculites are used, the polyoxocations are not stable and may hydrolyze almost completely to give gibbsite-type interlayer structures, while a regular pillar spacing also has been observed for clays in which the charge varies markedly from interlayer to interlayer, due to the capacity cited above of the oxocations to adopt variable charge through hydrolysis [106]. Moreover, clays with isomorphous substitution in the tetrahedral layers (beidellite) or F^- ions in the octahedral layers (fluorhectorite) form cross-linked clays, due to the formation of chemical bonds between the pillars and the surface oxygens [1].

Also the average size of the clay particles has a considerable influence on pillaring. Montmorillonites, which exhibit a pancake-shaped morphology and relatively large particles, give rise to well-organized pillared clays with the typical 1.8 nm spacing, due to a preferential face-to-face layer lamination (Fig. 7(A)). On the contrary, hectorite and its synthetic analog laponite, that have a lath-shaped morphology and extremely small particles, form amorphous materials (called delaminated clays), in which the particles are composed of only a few sheets in face-to-face aggregation and associated irregularly with preferential edge-to-face and edge-to-edge associations (Fig. 7(B)) [1,3,106].

These differences primarily lead to microporosity for pillared clays, as opposed to a combination of macro and microporosity for delaminated clays. It is worth noting that similar effects are also observed as a function of the drying method used. The pore structure is always smaller and regular for air-dried or spray-dried products than for freeze-dried products, regardless of which pillaring agent is used, due to long contact with liquid water throughout much of the first two drying processes [106].

Finally, the calcination process also plays a key role. Three general cases may occur: (i) the oxocations exit from the clay (no pillaring); (ii) the oxocations degrade in situ giving rise to layers of aluminum hydroxide (d=1.4 nm); (iii) in the case of a true pillaring, the oxocations dehydrate up to 573 K and dehydroxylate between 573 and 673 K. At higher temperatures, the pillars transform progressively, but the clays maintain the initial spacing of about

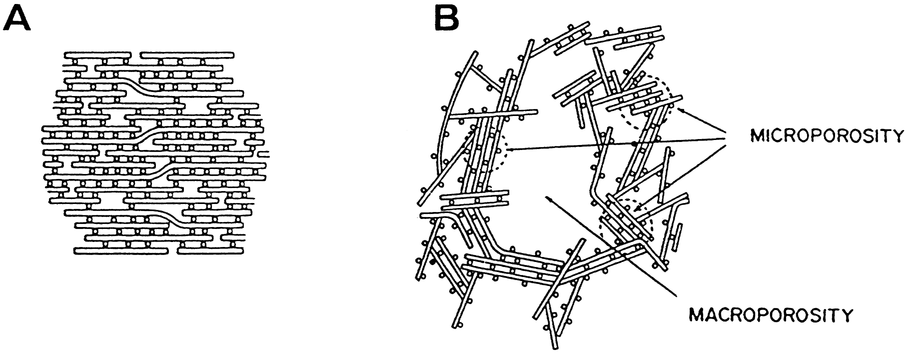

Fig. 7. Models for the layer association in (A) pillared clays and (B) delaminated clays containing polyoxocations of aluminum (open circles) [106,107].

1.9 nm, while at T>1073–1173 K, depending on composition, the clays degrade. The stability of pillared clays as a function of the calcination temperature depends on either the nature of the clay or the composition of the pillars. For example, an increase in stability may be achieved using mixed polyoxocations or by doping with small amounts of another element [1,3,109–114]. Furthermore, calcination produces protons, that may hydrolyze the cations in the octahedral sheets with a loss of aluminum.

This self-destruction is very important for acid clays, making the sheets brittle and reducing the dehydroxylation temperature, but it may be avoided by calcining in an NH_3-containing atmosphere [110,118]. However, in the pillared clays calcined at T>673 K, Lewis acidity is predominant, while the ratio Lewis/Brønsted sites depends considerably on the type of clay. The high Lewis/Brønsted ratio of delaminated laponite is indicative for an alumina-covering, while the acidity of pillared beidellite is very close to that of wide pore zeolites such as HY [1].

On the basis of the above considerations, it is clear why PILC's are of wide interest for catalytic applications. They are generally less active than starting clays in reactions conducted up to 523 K, although it may be relatively simple to regenerate activity [11,116]. However, it is in the area of reactions at high temperature that PILC's have been investigated the most, mainly for typical reactions of interest to the refining industry, due to their very considerable thermal and hydrothermal stability [109–111]. However, in concluding this brief survey of pillared cationic clays, we would like to cite two applications, which in our opinion seem to be very promising: the synthesis in soft experimental conditions of fine chemicals and the SCR of NO.

Important examples of the first class of reactions can be found in the references cited [29,109–111]; among these applications, of particular importance is the synthesis of durene, raw material to produce pyromellitic anhydride and, from it heat-resisting polymers [119,120]. In regard to the second class of reactions, it must be noted that different PILC's (containing Zr, Cr, Fe, Al or Ti) have been investigated and claimed as a promising new class of catalysts for SCR applications, due to their high activity and the potential poison resistance [121]. Furthermore, in a recent paper [122] it has been reported that PILC's can be useful catalyst supports for this reaction via comparison with other copper containing catalysts, it was shown that a PILC containing 3% copper, introduced by ion exchange, allowed operation in a wider range of reaction temperatures, due to the reduced rate of side ammonia combustion.

4.2. *Pillared anionic clays*

To prepare pillared layered anionic clays (PILAC's) large, highly charged anions are required, because the charge in the interlayer space must be negative. Large anions impart large expansion of the interlayers, while a high charge decreases the interlayer population, thus providing access to the interlayer surface for other guest-species [9]. It must be pointed out that even though many different anions have been claimed as pillaring agents (for example organic anions [44,128–131] or metal complexes [132–134]), only the increases in basal spacing have been reported, without any data on the surface area and porosity, i.e. on the presence of free and accessible space in the interlayer regions. Clearly, this does not mean that these compounds are less interesting from both the scientific and industrial points of view, but the use of different terms (such as intercalated or substituted) would be more suitable to avoid misunderstandings.

PILAC's may be classified in various ways, for example on the basis of the type of pillaring anion present (Table 7): (i) isopolyanions (or isopolyoxometalates); (ii) heteropolyanions (or heteropolyoxometalates) with a Keggin structure; and (iii) ferro or ferricyanides. It should be noted that, notwithstanding the low negative charge (see later), anionic clays containing ferro or ferricyanides also may be consid-

Table 7
Values of $d_{0\,0\,1}$ spacing and surface area for some pillared anionic clays [123–127]

Anionic clay	Pillaring agent	$d_{0\,0\,1}$ spacing (nm)	Surface area (m^2/g)
Zn/Al	$V_{10}O_{28}^{6-}$	1.19–1.23	169
Li/Al	$V_4O_{12}^{4-}$	0.95	—
Mg/Al	$Mo_7O_{26}^{6-}$	1.22	71
Zn/Al	α-$(H_2W_{12}O_{40})^{6-}$	1.46	63
Zn/Al	α-$(SiV_3W_9O_{40})^{7-}$	1.46	155
Mg/Al	$PV_3W_9O_{40}^{9-}$	1.20	136
Mg/Al	$Fe(CN)_6^{4-}$	1.10	246
Mg/Al	$Fe(CN)_6^{3-}$	1.10	235

ered as pillared clays, since the requirements of an increase in d-spacing, surface area and interlayer accessibility are fulfilled. PILAC's are not simple to prepare for the following reasons:

1. Exchange in anionic clays is more difficult than in smectite-type clays, because of the higher charge density or number of charges per unit of surface area, (higher or equal to 4 e^-/nm^2 instead of about 1 e^-/nm^2). The high charge density creates strong electrostatic forces between the brucite-type sheets and the anions, with consequent "stuffing" of the interlayers by the anions themselves, mainly when their charge is in the range -1 to -3 [17,126].
2. Hydrolysis of the pillaring anions can be caused by the anionic clays, as a function of the nature of the cations present in the brucite-type sheets.
3. Anionic clays may decompose in the synthesis conditions, chosen on the basis of the stability of the pillaring agents.
4. Carbonates compete with the pillaring anions, readily giving rise to mixed phases, due to their high affinity with the positively charged cationic sheets.
5. The anionic clay structure is stable only at relatively low temperatures.

All the above factors restrict the choice of the starting anionic clays, the pillaring agent, the preparation conditions and field of application. PILAC's may be prepared by different methods: (i) exchange of inorganic anions, (ii) exchange of organic anions, (iii) structure reconstruction, and (iv) direct coprecipitation [9]. In some cases, these methods have been combined in order to obtain more crystalline and ordered phases. For example, Dimotakis and Pinnavaia [58] used structure reconstruction of meixnerite, carried out in the presence of glycerol as a swelling agent, to produce anionic clays containing long-chain organic anions (e.g., adipate or toluenesulfonate), which afterwards were exchanged with the polyanions. Meixnerite was prepared by calcining a Mg/Al precursor at 773 K for 3 h and then slurrying the resulting mixed oxide in degassed water at 298 K under a nitrogen atmosphere. The PILAC's produced using this method are claimed to be more ordered and crystalline than those obtained with the other techniques.

PILAC's (as well as the intercalated clays) have been prepared with the aim to create new useful networks for shape selective adsorption or catalysis. In the field of catalysis, their preparation has been claimed in order to fulfill the following objectives: (i) to obtain shape-selective chemical, electrochemical or photo-catalysts, (ii) to stabilize homogeneous or biomimetic catalysts in order to increase their service life and allow easy recovery and recycling, or (iii) to prepare supported catalysts with concentrations of the active phase and activities higher than those obtained with conventional supports. Generally, PILAC's have been investigated mainly at relatively low temperatures, however some applications have been reported at temperatures at which serious doubts exist regarding their stability; then PILAC's must be more correctly considered as an alternative way to prepare homogeneous mixed oxides [9].

Unlike for anionic clays, there is little information in the literature on the thermal evolution of PILAC's, furthermore, the data which have been reported are not always in agreement and different interpretations and/or hypotheses have been made, probably as a result mainly of the different techniques employed or insufficient characterizations. Among the different types of PILAC's, up until now only those containing iso and heteropolyanions have been investigated. For example, it has been reported that the interlayer space provides a reactive environment for oxovanadates, that upon gentle thermal treatment (T>433 K) form at first, chain-like metavanadate species and then at higher temperature vanadates and oxides, while oxovanadates supported on alumina are stable up to 723 K [127,135].

Analogously, the heteropolyanions in the PILAC's show decomposition temperatures significantly lower than those of the corresponding salts with large counterions, that may be attributed to a reaction of the mixed oxides obtained by dehydroxylation of the brucite-type sheets with the Keggin ions [136,137]. On the other hand, it seems evident that the thermal stability of anions such as phthalocyaninetetrasulfonates, porphyrintetrasulfonates or metal complexes is not significantly modified by intercalation in the anionic clays and these compounds may be used only at low temperatures ($\leq$333 K).

On the basis of the above considerations it is evident that PILAC's (as well as intercalated clays) may have only low temperature applications as such. Furthermore, at present they have been investigated only on a laboratory scale. PILAC's containing iso or heteropolyanions have been investigated in photoxidation reactions, evidencing significant increases in activity, despite the scattering of the host particles [125,137]. Therefore, the realization of shape selective photochemical processes by controlling the pore size between the pillars, such as in zeolite may be hypothesized. The ability of HT compounds to incorporate anionic species while preserving their photochemical behavior has also been reported for ruthenium complexes [138].

Finally, we should like to cite the interesting results obtained using phthalocyanins intercalated in anionic clays in waste water purification treatments at room temperature. An increase in both activity and stability, together with the possibility to recover the catalyst simply by filtration was found [133,139].

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