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Ti-PILLARED CLAYS: SYNTHESIS AND GENERAL CHARACTERIZATION

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Abstract—This review is concerned with the synthesis and physical-chemical characteristics of a specific type of modified clay material: Ti-PILCs. The two general synthetic procedures and the main problems associated with the scale-up synthesis of these pillared materials are discussed in detail. The general characteristics of Ti-PILCs in terms of basal spacing, pillar homogeneity, surface area, microporosity, mesoporosity, pore size and distribution, thermal resistance and acidity are discussed in depth. Likewise, the most important synthesis parameters that have a clear and marked influence on the final characteristics of the materials are summarized.

Key Words—Alkoxide, Clays, PILCs, Review, Synthesis, $TiCl_4$, Titanium.

INTRODUCTION

Pillared clays (PILCs)

The escalation of oil prices in 1973 confronted the oil industry with the problem of how to maximize the processing of crude oil, especially the heavy fractions, to give gasoline components. Strong impetus was thus given to the development of catalysts with relatively large pore sizes, which were able to deal with larger molecules than the existing molecular sieves, and with good thermal and hydrothermal stability. The oil embargo in 1973 therefore acted as a stimulus for the investigation and development of PILCs (Vaughan, 1988).

The synthesis of metal oxide-pillared clays was first reported in the 1970s (Brindley and Sempels, 1977; Lahav *et al.*, 1978; Rees *et al.*, 1980; Vaughan *et al.*, 1979) and has been the subject of numerous studies since then (Arfaoui *et al.*, 2005a; Bahranowski *et al.*, 1998a, 1998b; Burch, 1988; Figueras, 1988; Kloprogge, 1998; Maes *et al.*, 1997; Pinnavaia, 1983; Sun *et al.*, 2006; Yamada *et al.*, 1991). These materials contain metal oxide pillars that sustain the clay sheets and lead to the formation of a bi-dimensional porous network.

The use of inorganic hydrated polyoxocations as pillaring agents provided thermally stable pillared clays with large specific surface areas (Kloprogge, 1998). Several single and mixed-oxide pillars have been prepared using polycationic species of Al, Zr, Ti, Fe and Cr, amongst others (Burch and Warburton, 1986; Cañizares *et al.*, 1999; Kloprogge, 1998; Sterte, 1986, 1991; Yamanaka and Hattori, 1988). Properties such as acidity, surface area and pore-size distribution of PILCs offer new shape-selective catalysts that are similar to the zeolites. Nevertheless, the thermal stability of these systems, which is less than that of zeolites, limits their use as catalysts to specific reactions that are performed at relatively low temperatures.

Layered silicates of the smectite group, especially montmorillonite, beidellite, hectorite and saponite, are naturally occurring clays that are commonly utilized in the preparation of pillared clays due to their low charge density and their swelling ability (Cañizares *et al.*, 1999; Cheng, 1999). Other than the smectite clays, pillared derivatives of a different clay ('rectorite') with a thick basal layer have been prepared (Guan *et al.*, 1986) and these materials have thermal and hydrothermal stability similar to that of faujasite zeolites.

The preparation of PILCs is based on the swelling properties of smectites and involves the compensation of the clay layer charge by large polymeric and oligomeric hydroxymetallic cations formed by hydrolysis of metallic salts. The reaction between the polycations and the clay, which involves the substitution of the exchangeable cations in the interlayer space of the clay by the inorganic polyoxocations, is usually known as a 'cationic exchange reaction'. Such an exchange can be easily accomplished by swelling the clay in any suitable polar solvent to form a suspension and mixing the desired replacement cations with this suspension. After the reaction, the resulting suspension is separated and washed to give the intercalated clay. The calcination of this material at a moderately high temperature leads to their dehydration and dehydroxylation resulting in oxidic pillars bound to the layers. Depending on the pillar species used, the resultant PILCs have interlayer-free spacings that are expanded to 4–20 Å and surface areas of 200–400 m^2/g. The pore size of PILCs depends on the calcination temperature; at high calcination temperature (>700ºC) the microporous structure collapses and results in large pores, whereas PILCs calcined at 400–600ºC behave as bidimensional molecular sieves (Tichit *et al.*, 1985).

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A wide variety of factors can influence the intercalation/pillaring process. This situation makes comparison of the results obtained by different authors difficult and leads to non-reproducible results. These factors include the nature of the host clay used as the parent material, the nature of the metallic cation, the hydrolysis conditions (concentration, time and ageing), the reaction time, the synthesis temperature and, finally, the washing, drying and calcination processes. In summary, the final properties of the PILCs depend heavily on synthesis conditions and on the thermal history of each sample.

Ti-pillared clays (Ti-PILCs)

Ti-pillared clays are solids that present an ordered arrangement in their structure and have a basal spacing of ~25 Å. These materials have a structure that consists of sheets separated by TiO_2 particles that are small but sufficiently large to allow the adsorption of different compounds.

Research on Ti-PILCs was initiated by Sterte (1986) who first reported the synthesis of Ti-pillared montmorillonite using $TiCl_4$ in hydrochloric acid solution. Ti-PILCs are synthesized by charge compensating the original cations of the host clay with large Ti polyoxocations which are produced by hydrolysis of different metal oxides or salts. After calcination, the polymeric cations are transformed into titanium oxide (TiO_2). Thus, the formation of Ti-PILCs can be described as the fixing of TiO_2 inside the clay to give the final product. Einaga (1979) demonstrated that the polymeric species are probably linked by Cl bridges $(TiO\text{-}Cl...TiOCl)_n$ and suggested the existence of $[(TiO)_8(OH)_{12}]^{4+}$ species, although the complex structure was not determined.

In spite of the interesting catalytic properties of Ti-based catalysts, Ti-PILCs have received considerably less attention than other pillared clays. Among the pillared clays, Ti-PILCs have the following remarkable characteristics: (a) greater interlayer spacing [~16 Å *vs.* ~10 Å for Al-PILCs or Zr-PILCs (Lahav *et al.*, 1978; Yamanaka and Brindley, 1979)], (b) high thermal and hydrothermal stability, which is comparable with that of Al-PILCs and Zr-PILCs (Sterte, 1986), (c) large pore sizes that allow further incorporation of active species without hindering pore diffusion (Cheng *et al.*, 1996), (d) intercalation of TiO_2 between the SiO_2 tetrahedral sheets is probably the best way to obtain a pillared clay with high values of both surface area and acidity (Yang and Chen, 1995) and (e) Ti-PILC-based catalysts have proved to be excellent for the selective catalytic reduction (SCR) of NO by NH_3 or hydrocarbons (Bahranowski *et al*., 1999; Li, W. *et al.*, 1997; Yang and Chen, 1995), with their activity slightly decreased by H_2O and SO_2. This behavior is different from that of Cu-ZSM-5, which is strongly deactivated by H_2O and/or SO_2 (Cheng *et al.*, 1996; Kato *et al.*, 1981).

Titanium chemistry is very complex. Titanium has been known for quite some time to form polymeric species in solution (Nabivanets and Kudritskaya, 1967). Several factors can affect Ti hydrolysis and polymerization and, therefore, influence the final characteristics of the Ti-PILC. Bernier *et al.* (1991) studied the influence of temperature on Ti-PILC by hydrolysis of $TiCl_4$ with HCl. Several authors (Khalfallah Boudali *et al.*, 1994; Nabivanets and Kudritskaya, 1967) have prepared Ti-pillared montmorillonite by intercalating polymeric cationic species by hydrolysis of $TiCl_4$ with HCl and H_2SO_4. Those authors carried out detailed studies on the experimental conditions for the hydrolysis of $TiCl_4$ with HCl. It was found that the physicochemical properties of pillared clays depend on several synthesis parameters, including the concentration of the metal ion and the method of preparation. Yamanaka *et al.* (1987) reported intercalation with $Ti(OC_3H_7)_4$ hydrolyzed in the presence of HCl. The same procedure was used by Choudary *et al*. (1990b). Del Castillo *et al.* (1997) studied the affect of the nature of the Ti alkoxides and the nature of acid used in the hydrolysis step. Finally, Valverde *et al.* (2002, 2003) reported the synthesis of Ti-PILCs by varying the nature of the Ti precursors hydrolyzed by HCl. These different methods proved to be suitable for the preparation of Ti-PILC.

Recently, new methods have been developed to prepare Ti-PILCs. Yoda *et al.* (2004) prepared Ti-pillared montmorillonite using supercritical CO_2: firstly, alkyltrimethylammonium cations were exchanged with interlayer cations in aqueous solution and, secondly, Ti isopropoxide dissolved in supercritical CO_2 was intercalated by hydrolysis with adsorbed water present in the interlayer space. The advantages of microwave dielectric heating were exploited recently in the synthesis of pillared clays (Fetter *et al.*, 1997, 2003; Gabriel *et al.*, 1998; Martinez-Ortiz *et al.*, 2003; Monsef-Mirzai *et al.*, 1999).

Applications of pillared clays

The main studies aimed at the application of pillared clays have, not surprisingly, concerned heterogeneous catalysts. It was found that if the cationic species itself was catalytically active, the resultant PILC would also be catalytically active. Additional applications have been found in fields as diverse as environmental uses, thermal insulators, pigments, electrodes and membranes (Arfaoui *et al.*, 2005b; Purnell, 1990; Serwicka and Bahranowski, 2004; Vercauteren *et al.*, 1997).

These materials are very active in cracking processes and demonstrate significant selectivity for larger product molecules (Adams, 1987). In this respect, a special issue of the journal *Catalysis Today* was published (Burch, 1988) and a review written by Figueras (1988). However, the original aim of using these materials as catalysts for FCC (fluidized catalytic cracking) was unsuccessful due to their poor hydrothermal stability. Nevertheless, the investigation of PILCs has continued, especially with respect to their applications in organic

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reactions catalyzed by acids (Corma, 1997; Occelli *et al.*, 1985) as well as other types of functionality endowed by the pillar species.

The PILCs with large surface areas can also be used as supports for metal catalysts to achieve homogeneous dispersion, increased adsorption area of reactants and shape selectivity. The pillar itself may incorporate a second functionality in catalytic reactions. The use of clays pillared with transition metal oxides has been extended to reactions such as dehydrogenation of cyclohexane to benzene, the Fischer-Tropsch synthesis, hydrotreatment, selective catalytic reduction (SCR) of NO, and selective organic transformations.

Specifically, Ti-PILCs have been tested in various processes such as the transformation of *m*-xylene (Molina *et al.*, 1994), the selective dehydration of 1-phenylethanol to 3-oxa-2,4-diphenylpentane (Gil *et al.*, 1996), the hydroxylation of phenol (Del Castillo *et al.*, 1996), the epoxidation of allylic alcohol (Choudary *et al.*, 1990a, 1990b; Khalfallah-Boudali *et al.*, 2000) and the SCR of NO by NH_3 or hydrocarbons (Chae *et al.*, 2004; Chmielarz *et al.*, 2004a, 2004b; Khalfallah-Boudali *et al.*, 2005; Yang *et al.*, 1998).

The objective of the present work is to report the main findings concerning the synthesis and characterization of Ti-pillared clays. The influence of the different parameters on both the preparation of these materials and the resulting physical properties are reviewed.

SYNTHESIS OF Ti-PILLARED CLAYS

In general, two different methods to create Ti complexes suitable for pillaring processes have been reported in the literature (Bovey *et al.*, 1996; Kooli *et al.*, 1997; Lin *et al.*, 1993). The first approach to the preparation of Ti complexes in solution is the addition of $TiCl_4$ to HCl, followed by dilution with distilled water and ageing for several hours prior to use as a pillaring agent (Bernier *et al.*, 1991; Ramos-Galvan *et al.*, 1997; Sterte, 1986; Yang *et al.*, 1992). The second approach is based on the hydrolysis of Ti alkoxides in HCl solution (Choudary *et al.*, 1990b; Fantan-Torres *et al.*, 1992; Malla *et al.*, 1989; Martinez-Ortiz *et al.*, 2003; Valverde *et al.*, 2002, 2003). Both methods have proven to be suitable for the preparation of Ti-PILCs although the first approach requires careful handling of the $TiCl_4$. A modification of the second method, using supercritical CO_2, has been developed for the synthesis of PILCs. This route consists of two steps: (1) the hydrophobitization of the interlayer space of the clay using an organic ion-exchange method with interlayer cations in aqueous solution; and (2) the intercalation of a metal alkoxide dissolved in supercritical CO_2 followed by hydrolysis with adsorbed water present in the interlayer space (Yoda *et al.*, 2004).

The first step in the synthesis of PILCs (although not always performed if the clay is naturally refined) is the purification of the natural clay to reduce the content of quartz, cristobalite and organic impurities. This step can be achieved, for example, by means of conventional sedimentation techniques (Bernier *et al.*, 1991). Subsequently, the purified clay is sometimes exchanged, generally with aqueous NH_4OH (or NaCl), to provide materials of uniform exchange properties. The exchanged clay then has to be washed in order to remove excess ions (Na^+, NH_4^+ and OH^-). Next, the clay is suspended in a polar solvent (generally water) and kept at room temperature for several hours to swell the clay.

The first procedure to prepare Ti-PILCs consists of adding $TiCl_4$ to a solution of HCl, which can be diluted with deionized water under vigorous stirring to obtain a final solution with a certain Ti concentration (generally ~1 M). This solution has to be aged for several hours prior to use.

The second procedure involves the preparation of a pillaring agent solution using an appropriate Ti alkoxide, which is hydrolyzed in HCl or CH_3COOH solution (Kitayama *et al.*, 1998; Ooka *et al.*, 2004). The resulting white slurry can be aged for 3−8 h with stirring at room temperature or at a given temperature (usually in the range 50−80ºC) to obtain a titanium sol (Ti^{4+} sol) solution. Different Ti alkoxides have been used: tetra-isopropoxide (Martinez-Ortiz *et al.*, 2003; Ooka *et al.*, 2003), methoxide, ethoxide, butoxide (Valverde *et al.*, 2003). Tetra-*n*-butyl titanate has also been used as the Ti precursor (Sun *et al.*, 2006).

The subsequent step involves exchange of the cations located between the clay layers with the previously formed Ti oligomers. The pillaring Ti solution is then added dropwise to the clay suspension followed by ageing at room temperature for 10−15 h. The solid then has to be separated from the solution by centrifugation and washed with deionized water. The aim of the washing stage is to remove excess Cl^- ions, which prevent diffusion of the polyoxocations within the interlayer spacing (Pesquera *et al.*, 1991). The solid may subsequently be air dried in a furnace at low temperature (30−60ºC).

Finally, the material has to be calcined. Generally, the calcination temperature is <500ºC. In some cases the pillared material can be hydrothermally treated before calcination and this is generally performed using an autoclave (Ooka *et al.*, 1999). The treatment temperatures and times are usually in the range 200−300ºC and 1−24 h, respectively. The aim of the hydrothermal treatment is usually to increase the catalytic activity of the pillared materials due to the crystallization of the TiO_2 pillars to anatase without altering the porosity.

In general, most authors synthesized Ti-PILCs using one of the procedures outlined above. The differences between the processes consist of the variation of synthesis parameters such as: Ti concentration of the solution resulting from adding $TiCl_4$ to HCl; concentra-

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tion of the HCl solution; HCl/Ti molar ratio; temperature at which the pillaring solution is prepared; clay suspension concentration; mmol of Ti/g of clay ratio; and calcination temperature.

GENERAL CHARACTERIZATION OF Ti-PILCS

Ti-PILCs are materials with large micropore areas and basal spacings in the range 20−25 Å. A specimen for examination by X-ray diffraction (XRD) in the low-angle range must be prepared by spreading the wet catalyst onto a glass slide and drying in air. An XRD spectrum of a Ti-PILC, synthesized using a purified bentonite (particle size <2 μm), consisting of montmorillonite in its Na-form, cation exchange capacity (CEC) of 94 meq/100 g of clay and chemical analysis (wt.%): SiO_2, 52.22; Al_2O_3, 16.81; Fe_2O_3, 3.84; Na_2O, 1.26; MgO, 0.88; CaO, 0.74; K_2O, 0.80 is shown in Figure 1a. It shows broad bands rather than sharp peaks, indicating the semi-crystalline nature of Ti-PILCs. The XRD spectrum usually has a diffraction peak at very low values for the 2θ angle; these are due to the basal reflection of the silicate layers (reflection from the (001) plane) and are typical of pillar formation (Ooka *et al.*, 2004). A second peak at higher values (6−8º2θ) is also detected in some cases (Del Castillo *et al.*, 1997; Valverde *et al.*, 2002). The assignment of this second peak to a polynuclear Ti species that is smaller in size (this leads to a lower degree of opening of the clay layers) is supported by the presence of the peak characteristic of the raw clay and by the variation of the intensity of these peaks during thermal treatment (Valverde *et al.*, 2002): upon increasing the calcination temperature, the intensity of the 001 reflection increases, whereas that in the 6−8º2θ range decreases. This has been ascribed to the polymerization of the Ti polyoxocations, to the existence of different hydration states, to the loss of adsorbed water of hydration (Del Castillo *et al.*, 1997), and even to the different structures of Ti oxide (Wahlbeck and Gilles, 1966) − all of which could generate a more homogeneous pillar distribution. The absence of the peak at 6−8º2θ would indicate that the material is reasonably oriented and has a good pillared structure (Ooka *et al.*, 1999, 2003, 2004). In summary, a proportion of the oriented silicate layers seem to show a basal reflection, and the partially disordered structure caused by delamination could weaken the basal reflection and give rise to higher-order reflections.

The interlayer spacing of the pillared clays is calculated by subtracting the thickness of the silicate layer (9.6 Å) from the basal spacing of the 001 reflection. This parameter is not generally affected by calcination temperatures of <500ºC, which suggests that the Ti species are deposited principally between the silicate layers (Yamanaka *et al.*, 1987). However, it is conceivable that some of the Ti polymers remain at the morphological surface of the clay crystallites. At ~600ºC a significant decrease in the basal spacing values generally occurs due to the collapse of the clay structure.

X-ray diffraction measurements over a wide-angle range provide information on the crystalline state of the TiO_2 pillar (Figure 1b). The crystalline size of TiO_2 could be calculated from the integral width of the anatase 101 diffraction (~25−26º2θ) using Scherrer's equation. This calculation would not be justified for fairly crystalline TiO_2 (anatase and possibly rutile), which suggests the presence of extra titania in the structure (example in Figure 1b). A number of authors have synthesized Ti-PILCs, the estimated basal spacing of which is in close agreement with the corresponding crystalline size of TiO_2 (Ooka *et al.*, 2004) and other authors have found the particle size of the TiO_2 pillar to be greater than the basal spacing (Shimizu *et al.*, 2002; Sun *et al.*, 2006).

The surface areas of pillared clays are typically obtained by applying the BET equation to the N_2 adsorption isotherm. Textural analyses of Ti-PILCs have shown that BET surface areas are in the range

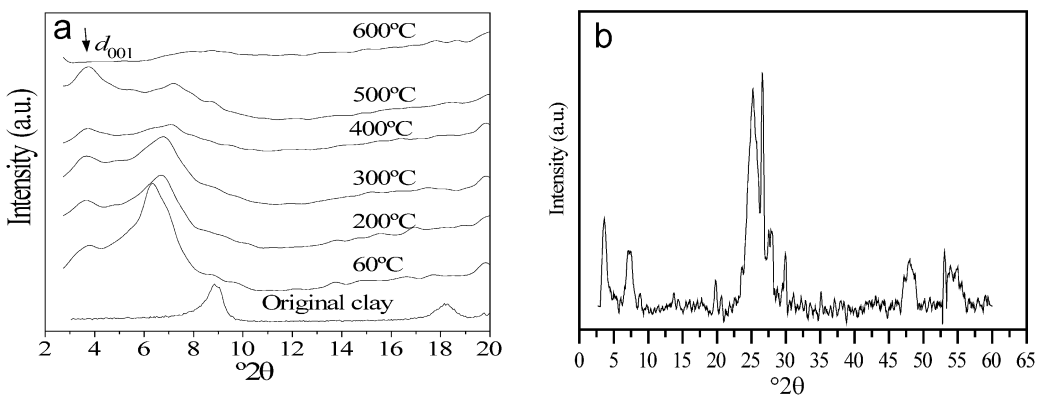


Figure 1. (a) General XRD patterns in the low-angle range of a Ti-PILC calcined at different temperatures (Valverde *et al.*, 2003); (b) XRD pattern of a Ti-PILC calcined at 400ºC.

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200−400 m^2/g. The specific surface area of the initial clay is generally small (<100 m^2/g) and, therefore, the large surface areas of Ti-PILCs indicate successful pillaring. This characteristic also indicates that TiO_2 pillars are intercalated into the silicate layers of the clay and that Ti deposited on the outer surface of the clay in the form of a separate anatase phase is probably not predominant (Chmielarz *et al.*, 2004a; Shimizu *et al.*, 2002). Thermal treatments to transform the polycations into oxide pillars below 500ºC do not usually affect specific surface areas and so it is possible to ensure that Ti-PILCs exhibit good thermal stability (Arfaoui *et al.*, 2006; Bernier *et al.*, 1991; Khalfallah-Boudali *et al.*, 1994; Sterte, 1986; Yamanaka *et al.*, 1987). In most cases the specific surface areas of Ti-PILCs decrease after calcination but remain above 200 m^2/g at 500ºC. This decrease in surface area has been related to the dehydroxylation of the clay and Ti pillars, but not to the sintering of the Ti pillars (Del Castillo, 1993). According to Zhu *et al.* (1995), the reduction in the surface areas and micropore volumes in PILCs upon increasing the calcination temperatures could be due to changes in the Hoffman Klemen effect, *i.e.* heating causes irreversible migration of small cations to the vacant octahedral sites in the clay layers and partial collapse of the structure occurs. According to Valverde *et al.* (2002, 2003) the main reason for the reduction in the surface area (mainly the microporous area) at high temperatures is the dehydroxylation and sintering occurring within the structure of the pillared clays. Both the BET surface area and total pore volume of Ti-PILCs are usually markedly reduced at temperatures of 600ºC or more. Thus, the porous structure is destroyed upon calcination at temperatures above 600ºC (Ooka *et al.*, 1999; Valverde *at al.*, 2003).

Although the forms of the isotherms for Ti-PILCs are a little different from one another, representative N_2 adsorption/desorption isotherms of Ti-PILCs are shown in Figure 2. The shape of the isotherm corresponds to type IV (Kooli *et al.*, 1997; Kostoglod *et al.*, 1998; Ooka *et al.*, 2004; Sychev *et al.*, 2000) according to the Brunauer, Deming, Derning and Teller (BDDT) classification (Sing *et al.*, 1985); such an isotherm is characteristic of solids including both micro- and mesopores. According to Gil *et al.* (1994), two different types of micropores of different size can be present in PILCs: ultramicropores (filled with N_2 at lower relative pressure) and supermicropores (filled at higher relative pressure). Ti-PILCs usually contain a significant amount of supermicropores (Valverde *et al.*, 2003). The presence of an H3-type hysteresis loop would indicate some degree of mesoporosity (slit-type mesopores). According to Hutson (1999), the mesoporosity arises from stacking defects inherent in the clay itself, as shown by the hysteresis loop seen in the adsorption isotherm of the unpillared clay (not shown). These stacking defects are the result of the attraction between negatively charged basal surfaces and positively charged crystal edges to form an internal 'house of cards' structure (Van Olphen, 1963). According to Maes *et al.* (1997), it is possible that a proportion of the TiO_2 particles do not penetrate the layer due to their polymeric character and they are deposited as a TiO_2 phase on the external surface of the clay layers. This coating could bring about a large amount of mesopores in the pillared material and this can be assessed if the pillared material exhibits a distorted isotherm with H1 type hysteresis, both of which are typical of corpuscular systems (oxide gel structures). According to Sun *et al.* (2006) the larger the size of the TiO_2 intercalated in the silicate layers the weaker the hysteresis isotherm.

The pillaring species are only responsible to a certain extent for the porosity; another important factor is the orientation of the clay layers (Maes *et al*., 1997). Clay layers can be stacked in a face-to-face, face-to-edge or edge-to-edge orientation depending on the layer size, the surface charge density and the interlaminar cation. The orientation of the clay layers is also influenced by the drying conditions; rapid drying fixes the random orientation of the clay tactoids, while slow drying favors a more ordered settlement of the tactoids.

The microporous structure of pillared clays is characterized by the distance between the clay layers and the distance between the intercalated oxides (pillars); these are the interlayer and interpillar spacing, respectively. The interlayer spacing depends on the chemical nature and the height of the intercalating

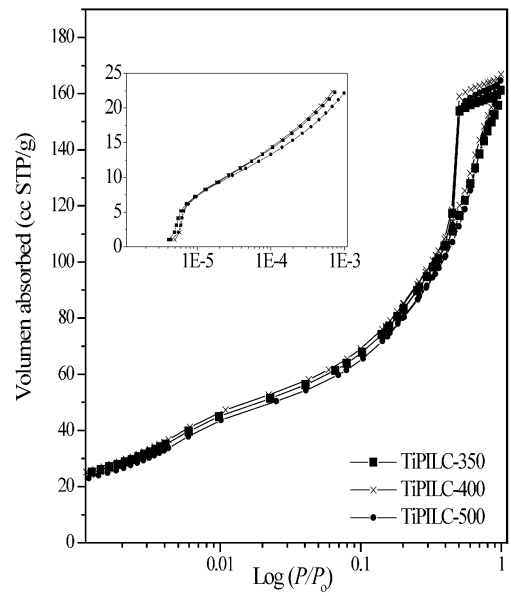


Figure 2. Nitrogen adsorption/desorption isotherms of a Ti-pillared clay calcined at different temperatures (Valverde *et al.*, 2003).

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species. On the other hand, the interpillar distance is mainly related to the density of pillars, *i.e.* the number of intercalating species introduced between the layers, which in turn depends strongly on the extent and the distribution of the charge density on the clay layers (Ge *et al.*, 1994) and also on the size of the pillars and the oligocation charge. Both interlayer and interpillar spacings can be modified during the calcination step of the synthesis procedure when phenomena such as elimination of organic parts of the polycations and dehydration or sintering of the pillars take place (Figueras, 1988; Sterte and Shabtai, 1987; Toranzo *et al.*, 1998). It has been proposed that it is the interpillar rather than the interlayer distance that controls the pore-size distribution of pillared clays (Yang and Baksh, 1991). This distance depends on the number of pillars introduced between the clay layers and this, in turn, is mainly related to the amount of exchangeable cations of the clay (CEC). Therefore, the CEC can be a key factor for the optimization of the synthesis procedure in order to obtain pillared clays with a desired population of pillars and controlled pore-size distribution (Suzuki *et al.*, 1991). On the other hand, the CEC of the clays is only partially compensated by the charge of the oligomers because some proportion of the exchangeable cations on the clay remains unchanged (Suzuki *et al.*, 1991). Besides, intercalation agents are usually prepared by partial hydrolysis of solutions of the cations and their size and polymerization degree is not always well established. All of these facts make it extremely difficult to calculate the effective charge of the pillars. This problem can be solved by measuring the residual CEC of the clays after pillaring with Ti species. The residual CEC provides an approximate estimation of the clay layer charges that are not compensated by positively charged Ti species (pillars and oligomers).

In many cases the Ti-PILCs microporous region contains a bimodal pore-size distribution (Gil *et al.*, 1994; Hutson, 1999; Hutson *et al.*, 1998; Valverde *et al.*, 2003). A wide mesopore size distribution is usually characteristic of this type of catalyst. According to Maes *et al.* (1997) the larger pores are probably due to the external mesoporous TiO_2 phase and are usually present in small numbers if the material is well pillared. However, it is not possible to talk about a general Ti-PILC pore-size distribution because, as mentioned above, this characteristic depends on many factors, such as drying or calcination conditions.

As far as thermal behavior is concerned, the low level of thermal stability is the common drawback associated with pillared clays. Ti-PILCs are stable materials at temperatures <500ºC. A representative TGA plot of a Ti-PILC (Figure 3) shows a defined weight loss <150ºC due to dehydration (loss of physically adsorbed water). A slight weight loss in the range 150−500ºC is attributed to the removal of excess water adsorbed within the pillared interlayer region and dehydroxylation of the pillars (Occelli and Tindwa, 1983). Dehydroxylation continues between 500 and 875ºC. As a result, only a small step is observed up to ~600ºC and this is related to the collapse of the clay layers (Bagshaw and Cooney, 1993). The dehydroxylation temperature can be related to the thermal stability of the pillared samples (Kurian and Sugunan, 2005; Valverde *et al.*, 2003).

The acidity of pillared clays originates from the clay layer, from the pillaring agent, or from an interaction between these two factors. The pillars are the main source of Lewis-type acidity, while a weak Bronsted acidity arises from structural hydroxyl groups of clay layers (Chevalier *et al.*, 1994; Chmielarz *et al.*, 2004b; Matsuda *et al.*, 1988). The NH_3 desorption spectra of pillared clays are complex. However, it is supposed that the low-temperature peak, centered at 150−190ºC, is mainly due to desorption of ammonia bound to weak Bronsted acid sites and physisorbed ammonia molecules, while high-temperature maxima can be attributed to desorption of NH_3 from Lewis acid sites. The NH_3 desorption spectrum of Ti-PILCs is typically spread in the temperature range 110−500ºC, indicating a high degree of strongly chemisorbed NH_3 that desorbs in the high-temperature region (T>250ºC) (Bernier *et al.*, 1991; Bagshaw and Cooney, 1993; Chmielarz *et al.*, 2004a). These materials are therefore characterized by greater Lewis acidity.

INFLUENCE OF THE MOST IMPORTANT SYNTHESIS PARAMETERS

The physicochemical properties of the pillared clays depend on several synthesis parameters, including the concentration of the metal ion, the temperature, the method of preparation and the nature of the host clay. For this reason, an extensive study concerning the most important synthesis parameters related to Ti-pillared clays will be given at this point.

Del Castillo (1993) demonstrated that the amount of Ti that can be intercalated as the appropriate polycation is related to the pH of the intercalation solution. A pH

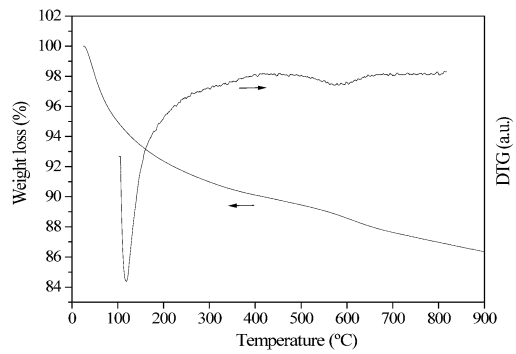


Figure 3. TG and DTG curves of a Ti-PILC (Valverde *et al.*, 2003).

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value >1 would increase the degree of polymerization and the Ti polycation exchange, whereas a pH value >1.8 should lead to Ti oxide precipitation. Khalfallah Boudali *et al.* (1994) found that the structural properties of the pillars obtained by varying the acid are due to the different natures of the polymeric cationic species. According to Valverde *et al.* (2002) the optimal HCl/Ti molar ratio to give Ti-PILCs with homogeneous pillar distribution and good textural characteristics is in the range 2−2.5.

On the other hand, the speed of addition of the pillaring solution to the clay suspension has been related to the homogeneity of the pillar (Valverde *et al.*, 2002) on the basis that the intensity of the 001 reflection increases at lower addition speeds. The influence of the speed of addition on the pillaring process has been explained in terms of the ion-exchange process. Thus, pillared samples with a low Ti content have been prepared with high addition speeds, meaning that it is possible to claim that the insertion of the hydrolyzed polynuclear Ti species as pillars is enhanced when a slow addition speed of the pillaring solution to the clay suspension is used. The contact time of the pillaring solution and the clay suspension has to be sufficient to achieve ion exchange (10−14 h) and this factor does not have a significant influence on the final characteristics of the resulting material in this time period.

The synthesis temperature is also an important parameter that can again be related to the extent of the ion exchange process as well as to the nature of the Ti species in solution formed at a given temperature. Several investigations have demonstrated that the pillaring process at room temperature (~20ºC) is the most suitable for the synthesis of Ti-PILCs (Bernier *et al.*, 1991; Valverde *et al.*, 2002; Vicente *et al.*, 2001). Valverde *et al.* (2002) found that Ti-PILCs synthesized at higher temperatures (60ºC) gave rise to a heterogeneous pillar distribution and a proportion of the raw clay remaining in the sample. Similar results were reported by Bernier *et al.* (1991) on using $TiCl_4$ as the Ti source. In the same way, the textural characteristics were worse and Ti contents lower in Ti-PILCs synthesized at temperatures below room temperature in comparison to pillared clays synthesized at room temperature.

Besides $TiCl_4$, different Ti alkoxides have been described in the literature as a source of Ti (Del Castillo *et al*., 1997; Mogyorosi *et al.*, 2003; Valverde *et al*., 2003; Vicente *et al*., 2001). These studies demonstrated that the properties of the alkoxide group, *e.g.* the length of the chain, can affect the ion-exchange process and, therefore, the structure of the pillars. According to Vicente *et al.* (2001), intercalation with $TiCl_4$ and $Ti(EtO)_4$ strongly affects the structure of the clays, not by acid attack on the octahedral sheet but through the disaggregation of particles (Vicente *et al.*, 2001). In general, $Ti(isop)_4$ has been found to be less aggressive to the clays.

The great influence of the polycation/clay ratio on the constitution and distribution of the pillars has been reported previously in the literature (Del Castillo *et al.*, 1997; Mogyorosi *et al.*, 2003; Sánchez and Montes, 1998; Sterte, 1986). In general, an increase in the amount of Ti source hydrolyzed and added to the clay suspension leads to an increase in the amount of TiO_2 incorporated between the clay layers that form the pillars. This in turn leads to an increase in the specific surface area of the material. Nevertheless, a very high level of Ti added in the pillaring procedure could negatively affect the physicochemical and textural characteristics. This fact has been ascribed to the intercalation of different Ti species between the clay layers (of different sizes) or bulk TiO_2 on the external surface (Valverde *et al.*, 2003).

The clay concentration in the suspension is a fundamental variable in the preparation of pillared clays on an industrial scale for moderate preparation volumes. The conventional synthesis of pillared clays requires a very dilute aqueous medium (Cañizares *et al.*, 1999; Del Castillo, 1993; Del Castillo *et al.*, 1997; Yoneyama *et al.*, 1989). In order to reduce the amount of water needed in the synthesis (*i.e.* to increase the amount of pillared clay obtained in each synthesis), samples involving more concentrated clay suspensions may be prepared (Pérez-Zurita *et al.*, 2005). In this way, the synthesis of PILCs from highly concentrated clay suspensions using a microwave oven has been reported (Monkaya and Jones, 1995) and the beneficial effects of ultrasound radiation in reducing the amount of water required has been investigated (Pérez-Zurita *et al.*, 2005). It is clear that the large amount of water used in the suspension preparation should require re-circulation of this resource. The use of acetone/water mixtures as the solvent has been reported as an alternative to increase the concentration of clay up to 30−50% (Storaro *et al.*, 1996, 1998). Unfortunately, the majority of the methods proposed in the literature are quite impractical for an industrial synthesis.

SCALE-UP SYNTHESIS

The proven applications of pillared clays in the fields of heterogeneous catalysis and adsorption, coupled with the small price of the raw material clays, have given rise to interest in the production of these materials on an industrial scale.

Most of the studies reported in the literature have been performed on pillared clays prepared on a laboratory scale, generally a few grams per batch. Studies of samples produced by scale-up preparation methods at the pilot level are almost non-existent in the open literature.

Over the past 15 years, considerable effort has been devoted to the standardization of procedures to produce industrial quantities of pillared clays. In order to scale up

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the process successfully it is necessary to understand the successive steps involved in the preparation of these materials. Intercalation is generally carried out in dilute systems in which a dilute homo-ionic clay suspension is brought into contact with a dilute intercalating solution. This requires the handling of large suspension volumes during the preparation and the washing steps. Vaughan (1988) indicated the importance of three prerequisites for the manufacture of commercial catalysts: (1) use of the whole clay, with minimal or no refining; (2) pillaring of the clay without prior cationic exchange; (3) use of large concentrations of clay and polycations. These prerequisites have been considered by several authors (Gil and Gandía, 2000; Molina *et al.*, 1992; Perez-Zurita *et al.*, 2005; Schoonheydt and Leeman, 1992). In summary, control of the concentration and the minimization of washing volumes enables a scaled-up process to be developed (De Stefanis and Tomlinson, 2006). A reproducible scale up has been achieved using much reduced quantities of water (Koch *et al.*, 2004). The large quantity of water required for clean up is a factor that is often overlooked in laboratory studies.

Problems related to the scale up of small pilot production of Al- and Al/Fe-pillared clays have been addressed (Kaloidas *et al.*, 1995). The catalytic properties of these pilot samples have been evaluated in several reactions, *e.g.* terpene conversion (De Stefanis *et al.*, 1994), SCR of NO (Perathoner and Vaccari, 1997) and hydroconversion of heptane (Moreno *et al.*, 1996). Valverde *et al.* (2003) verified that Ti-PILCs produced on a pilot scale exhibited the typical physical characteristics generally found for such materials; namely, specific surface areas >250 m^2g^{-1}, micropore volumes of 0.15 cm^3g^{-1} and thermally resistant pillars. These values were, however, noticeably less than those obtained with laboratory samples, especially after calcination at relatively high temperatures. These observations indicate that the pilot preparation could still be improved. However, in spite of the differences in their textural properties, from the catalytic point of view, laboratory and pilot samples show very similar catalytic performances in different tests (*e.g.* the SCR of NO over Cu ion-exchanged Ti-PILCs).

CONCLUSIONS

The aim of this review is to provide the reader with a general overview of the synthesis and physical-chemical characteristics of a specific type of modified clay material: Ti-PILCs. The two general synthesis procedures used to produce these pillared materials are described in detail: (1) hydrolysis of $TiCl_4$ by HCl or H_2SO_4; and (2) hydrolysis of different Ti alkoxides by HCl. Additionally, new specific methods (which are based on the two listed above) such as the use of supercritical CO_2 and the use of microwave dielectric heating are also mentioned.

The general characteristics of Ti-PILCs – basal spacing, pillar homogeneity, surface area, microporosity, mesoporosity, pore size and distribution, thermal resistance and acidity – are discussed in depth. Likewise, the most important synthesis parameters that have a clear and significant influence on the final characteristics of the materials are summarized (the most important results are highlighted).

Finally, the main problems related to the scale-up synthesis of pillared clays and the most important studies concerning this subject are also covered.

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