

Pillared Clays and Related Catalysts

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Miguel Angel Vicente
Editors

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Foreword by Thomas J. Pinnavaia

 Springer

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ISBN 978-1-4419-6669-8

e-ISBN 978-1-4419-6670-4

DOI 10.1007/978-1-4419-6670-4

Springer New York Dordrecht Heidelberg London

Library of Congress Control Number: 2010933724

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Printed on acid-free paper

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Foreword

The concept of using intercalation chemistry to transform a lamellar solid into a porous analog originated more than 55 years ago in the Aberdeen University laboratory of Professor Richard M. Barrer. In a seminal 1955 paper, co-authored with graduate student D.M. MacLeod and published in the *Transactions of the Faraday Society*, Barrer described how the “replacement of inorganic cations in montmorillonite by $\text{N}(\text{CH}_3)_4^+$ and $\text{N}(\text{C}_2\text{H}_5)_4^+$ cations opens up the lamellae and causes profound changes in the sorption and intercalation of organic molecules.” The paper also demonstrated sorptive selectivity based on the cross-sectional molecular diameters of the adsorbates. Despite the promising molecular sieving properties of Barrer’s alkylammonium ion-exchanged forms of smectite clays, his innovation remained essentially undeveloped for two decades due primarily to the concomitant discovery of synthetic zeolites Linde Type A (LTA) and Type X (FAU). These purely inorganic molecular sieves had surface areas and pore volumes comparable to Barrer’s clay intercalates, but they were far more thermally stable in comparison to the alkylammonium ion-exchanged forms of smectic clays.

In 1977, George W. Brindley and R.E. Sempels showed that the partial replacement of Na^+ -exchange cations by hydroxyaluminum cations in the galleries of the smectic clay beidellite afforded intercalates with nitrogen BET surface areas up to $500 \text{ m}^2/\text{g}$ after calcination at $325 \text{ }^\circ\text{C}$. This finding presaged the 1978 W.R. Grace patent invention of David E.W. Vaughan, Roger J. Lussier, and John S. Magee, Jr. on “Pillared Interlayered Clay Materials Useful as Catalysts and Sorbents.” This breakthrough garnered the attention of the clay and zeolites research communities and spawned a flurry of research activity that persists to the current day. To date, more than 3,500 journal publications and 390 patents have been published on pillared smectite clays and related porous derivatives of lamellar compounds. Moreover, the advances in the applications of pillared materials continue to expand. The decade following the pillared clay disclosure of Vaughan et al. witnessed the publication of approximately 200 journal articles and 64 patents. In the decade of the 1990s, the numbers grew to 1,300 journal articles and 170 patents. The decade following the turn of the twenty-first century saw a sustained interest in pillared materials, as evidenced by the publication of more than 2,000 additional journal articles and 155 patents.

The decade following 2010 almost certainly will witness continued research on the applications of pillared layered materials. For this reason the present volume on pillared intercalates is an exceptionally timely contribution that will serve as a valuable reference source. Much of the contemporary interest in pillared clays and related interaction compounds is stimulated by their properties as heterogeneous catalysts for the production of fine chemicals and as selective adsorbents for molecular preparations, environmental remediation, and pollution control. The present volume provides a thorough and expert accounting of the recent advances in each of these application areas. Emphasis is understandably placed on pillared versions of smectite clays and layered double hydroxides, also known as hydrotalcites or mixed metal hydroxides, in part, because these are the most versatile and cost-effective lamellar host structures available in commercial quantities for pillaring. In addition, detailed state-of-the art evaluations are also provided for layered phosphates and porous aluminum phosphates. The 16 complementary chapters cover a very broad range of catalytic and sorptive processes of environmental and industrial relevance with little or no redundancies. The level of coverage attests to the expertise of the contributing authors in the field of pillared layered materials. The book surely will serve as an essential reference source over the next decade for workers engaged in the intercalation chemistry and materials applications of lamellar inorganic solids, particularly layered oxides and hydroxides.

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Thomas J. Pinnavaia

Preface

The interest in all aspects related to pillared interlayered clays, such as new synthesis methods or the study of their properties and applications, has greatly increased over the last few years. Several of the papers devoted to pillared interlayered clays, both as articles and as book chapters, have reviewed various aspects of the preparation, characterization, or applications of these solids. The approach that has been commonly used in previous studies to organize such a large amount of information is mainly based on the preparation of pillared clays, as well as some aspects about the catalytic applications of these solids. As indicated earlier, the interest in these solids is so large that, since our first comprehensive review on the synthesis and catalytic applications published 9 years ago (Gil A, Gandia LM, Vicente MA (2000) Recent advances in the synthesis and catalytic applications of pillared clays. *Catalysis Reviews*, 42:145–212), more than 500 new references have appeared in the literature and interest in this field is continuously increasing. A second review deals with the porous structure developed by these materials during the intercalation process (Gil A, Korili SA, Vicente MA (2008) Recent advances in the control and characterization of the porous structure of pillared clay catalysts. *Catalysis Reviews*, 50:153–221). This is a very important aspect because the textural properties of pillared clays play a key role when these materials are used as catalysts, adsorbents, or in gas separation.

Since the first works introducing the aluminum intercalated clay family at the beginning of the 1970s, the synthesis of pillared interlayered clays has expanded enormously. The need for solids that could be used as cracking catalysts with larger pores than the zeolitic materials spurred the synthesis of new porous materials from clays. These solids are prepared by exchanging the charge-compensating cations present in the interlamellar space of the swelling clays by hydroxyl-metal polycations. On calcining, the inserted polycations yield rigid, thermally stable oxide species, which prop the clay layers apart and prevent their collapse. The intercalation and pillaring processes produce the development of a porous structure with the presence of particular surface sites. These properties determine the potential use of the solids in catalytic, purification, and sorption-based separation applications. The properties of pillared clays synthesized in the presence of microwave irradiation are compared to those prepared in the conventional way by Fetter and Bosch in

Chapter 1. In **Chapter 2**, Pires and Pinto present the potential use of pillared clays as selective adsorbents of natural and biogas components, such as carbon dioxide, methane, ethane, and nitrogen.

An important characteristic of the pillared clays is their acidity. The type, number, and strength of surface acid sites depend on several factors, such as the exchange of cations, the preparation method, and the nature of the starting clay. These are properties directly related to the catalytic performance. Therefore, the type of acidity can determine which type of reaction the clays can catalyze. Several types of reaction have been studied, such as alkylation, dehydrogenation, hydrocracking, and isomerization. Some examples of this type of applications are summarized in **Chapters 3** and **4**.

One of the most studied topics related to pillared clays is their use as supports for catalytically active phases, and the use of the resulting solids in several reactions, particularly in environment-friendly ones. The number of articles in this field is very extensive, including catalysts that contain Co, Cr, Cu, Fe, Mn, Ni, Pd, Pt, Rh, or V. Mishra summarizes the synthesis and applications of transition metal oxide-pillared clays in **Chapter 5**. Titanium, iron, chromium, manganese, and mixed oxides were considered, with emphasis on their future potential as catalysts. Hydrocarbon cracking and various examples related to environmental processes as photocatalysis and pollution control in gas and liquid phases are presented by the author. The use of pillared clays in catalytic waste water treatment is summarized in **Chapters 6–8**. Herney-Ramirez and Madeira reviewed the use of pillared clays in heterogeneous Fenton-like advanced oxidation processes. The effect of the main operating conditions on oxidation efficiency is considered by the authors. Special attention to the use of pillared clays in wet air catalytic oxidation (WACO), wet hydrogen peroxide catalytic oxidation (WHPCO), and photo-Fenton conversion of pollutants is considered by Perathoner and Centi. The catalytic wet peroxide oxidation of phenol using pillared clays in a continuous flow reactor is presented by Guélou et al. in **Chapter 8**. The experimental results are very promising for developing a catalytic continuous process for industrial wastewater purification. The chapter written by Zuo et al. reviews the recent developments offered from pillared clay-supported noble metals and metal oxide catalysts for complete oxidation of representative volatile organic compound (VOC) molecules such as benzene, toluene, chlorobenzene, phenol, among others. Selective reduction of NO_x has been the reaction *to* environmental interest for which pillared clays have been most widely used. Recent trends, limits, and opportunities offered from pillared clays and other related materials (layered clays, layered double hydroxides (LDHs), and porous clay heterostructures (PCHs)) in this field are discussed by Belver in **Chapter 10**. Special attention is focused on the modification that led to materials with a higher or comparable activity to that described by commercial systems. In **Chapter 11**, Vicente et al. presents the use of pillared clays in catalytic oxidation reactions related to green chemistry concepts.

The book also includes four Chapters (**12–15**) dealing with treatment of other layered materials, mainly anionic clays, and mesoporous solids, comparing them with the pillared clays. The state-of-the-art in the synthesis, characterization, and

catalytic performance of layered double hydroxides (LDH) with the hydroxalcite-type structure containing several polyoxometalates (POM) in the interlayer is presented by the Rives group in [Chapter 12](#). The immobilization of polyoxometalate species in the interlayers of layered double hydroxides with the hydroxalcite-type-solids allows the preparation of homogeneous catalysts with tailored redox and acidity properties. The authors indicate that the properties of these materials can be finely tuned through the modification of the cations in the brucite-like layers and the polyoxometalate in the interlayer, in order to apply them to several catalytic processes. Other parameters such as the polarity modulation or the solvents can modify the reactivity of the LDH–POM catalysts. In [Chapter 13](#), Figueras presents the latest ideas on the modification of the basic properties of hydroxalcites by anion exchange and on the properties of solid bases as catalysts. Several examples of applications are given, with emphasis on industrial processes recently shown such as isomerization of olefins, aldolization, oxidation of ketones; supports of metal catalysts; as well as adsorbents and anionic exchangers. The synthetic pathways for obtaining mesoporous phosphate structures and aluminophosphates make up the subjects presented in [Chapters 14](#) and [15](#) by Moreno et al. and O'Malley et al., respectively. The preparation of metal-supported catalysts and their application in gas separation, adsorption, and catalysis are also reviewed.

In the final chapter, the synthesis and application to industrial catalytic reactions of macrocyclic complexes supported on clays with thermal and chemical stability are presented by the team of Kumar et al.

The editors are very grateful to all the authors for their willingness to participate in this project, and for their enthusiasm in writing the contributions, and for sharing their knowledge with the readers.

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Chapter 1

Microwave Effect on Clay Pillaring

Geolar Fetter and Pedro Bosch

Abstract Pillared clays may be prepared in presence of microwave irradiation as it has been extensively used in organic chemistry syntheses. Preparation time of the conventional intercalating solution takes about 2 days, but only 15 min when the preparation mixture is microwave-irradiated. The amount of water required to disperse and to dilute the pillar precursor salts is also significantly reduced. In this work, the properties of the pillared clays prepared in presence of microwave irradiation are compared to those prepared by the conventional way. Their performance as catalysts or as adsorbents is discussed.

Keywords Clays · Montmorillonite · Pillars · Microwave irradiation · Microporous · Ion exchange · Adsorption · Catalysis · Aluminosilicate

1.1 Introduction

Catalysis and adsorption require materials with high porosity and large surface area. Although clays, as montmorillonite, present a surface area of ca. 40–70 m²/g and a porosity of ca. 0.006–0.010 cm³/g, which are low, their layered structure may be expanded through organic or inorganic pillars. Indeed, clays are cationic exchangers. The pillars may be large inorganic metalpolyoxocations intercalated between the aluminosilicate layers. These polyoxocations (Al, Zr, Cr, . . .) are, then, converted into stable metal oxide pillars through a calcination step, holding the layers permanently apart and, thus, creating microporosity. In this way, the interlamellar space, originally close to 3.0 Å, can reach a value as high as 20 Å. The porosity of the

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pillar-interlayered clays can be tailored by changing the size, shape, and concentration of the intercalated species [1–4]. The obtained surfaces and microporosity are ca. four times larger than the values of the non-pillared clay.

In this way, pillared clays may be used, for instance, in fine chemistry as catalysts in the synthesis of biologically active multifunctional dihydropyrimidinones [5]. In hydrocracking, chromia and tin oxide-pillared clays are performing as catalysts of heavy liquid fuels [6], while in photocatalysis, titania-pillared montmorillonite has been used to remove 4-chlorophenol in water and methanol in air [7]. Otherwise, clays may be intercalated with organic compounds such as drugs. The clay acts as a drug deliverer depending on the environmental conditions [8, 9].

Among the large number of clays, montmorillonite is the most frequently used in pillaring chemistry. Indeed, it is often found in nature and the cation-exchange capacity is high (50–150 mequiv/100 g of clay). Still, other smectite clays such as saponite [10, 11], beidellite [12, 13], nontronite [14], or hectorite [15, 16] have been pillared.

The pillaring process starts with the intercalation of metalpolyoxocations which are large complexes (ca. 10 Å) constituted by clusters of oxygen and metal atoms. The corresponding charge promotes the cation exchange and the subsequent interaction with the negatively charged aluminosilicate layer. For instance, the polyoxocation of aluminum is a Keggin ion, $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$, which contains 13 aluminum atoms and whose resulting charge is 7⁺.

The conventional preparation may be summarized as follows [2, 4]. A pillaring agent is initially prepared. Then, the suspended clay is mixed with the polyoxocation solution and maintained at ca. 80 °C for 18 h. After the intercalation process is complete, the clay is separated, washed, and then calcined (300–800 °C for 5 h), i.e., pillared. The obtained sample is often labeled as PILC (pillared clay).

Clearly, the conventional procedure is complex and time-consuming as shown in the following chapters. Furthermore, from an industrial viewpoint, in which large amounts of clay have to be prepared, this process may result uneconomic, since enormous equipments as well as the manipulation of huge volumes of water are required [17–19].

Irradiation during the solution preparation and the intercalation decreases significantly the polyoxocation formation time as well as the amount of water required as it is a source of external energy. Irradiation propitiates the required dispersion of cations in a more concentrated solution. During intercalation, it favors a fast diffusion of the exchanged species. Last but not least, irradiation may be used to dry the samples [20, 21] (Fig. 1.1).

Materials may be irradiated with a wide interval of wavelengths including microwaves. Microwaves are electromagnetic radiation, whose wavelength lies in the range of 1 mm to 1 m (frequency range of 0.3–300 GHz). Only narrow frequency windows centered at 900 MHz and 2.45 GHz are allowed for microwave heating purposes. The exact nature of microwave interaction with reactants during the synthesis is somewhat unclear and speculative. However, energy transfer from microwaves to the material is believed to occur through either resonance or relaxation, which results in rapid heating [22].

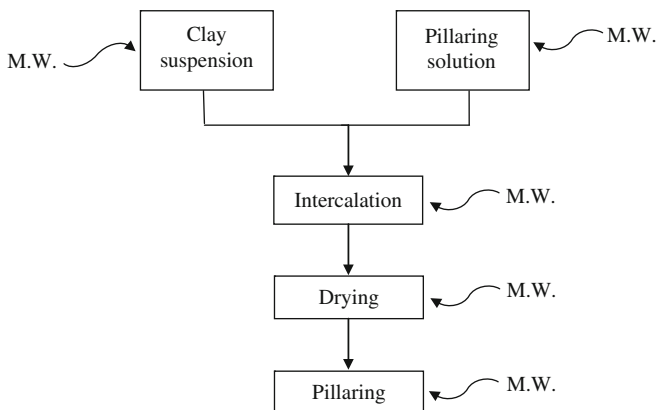


Fig. 1.1 Preparation steps of pillared clays where microwave irradiation can be applied

In this work we review and discuss the use of microwave irradiation on clay pillaring.

1.2 Experimental

Microwave equipment to irradiate typically consists of an autoclave of 500 ml, which fits in a microwave oven whose power may be selected. A stirring mechanism is adapted to the autoclave so that temperature is the same all over. The frequency is always 2.45 GHz. Temperature is controlled through an infrared radiation sensor. Pressure can reach values as high as 10 atm. Laboratory apparatus are commercialized by Milestone or CEM, among other; in our case, we have used a Sistemas y Equipos de Vidrio model MIC-II apparatus (see Fig. 1.2).

Still, reproducible results have been reported using domestic ovens [23–25] but, in order to avoid explosions, the obtained amount of sample has to be very small, around 5 g. As the samples cannot be stirred, the probability of high temperature points cannot be discarded.

1.3 Determinant Conditions

1.3.1 Irradiation Time

1.3.1.1 Alumina-Pillared Montmorillonite

Irradiation time is one of the most determining parameters on the sample features. Fetter et al. [25] studied the synthesis of Al-intercalated montmorillonites. If the prepared samples are irradiated for 2 min or more, during the intercalation

Fig. 1.2 Synthesis autoclave apparatus operated with microwave irradiation



step, and compared to the conventionally prepared materials (18 h), a higher surface area is obtained (340 vs. 244 m²/g). In the microwaved samples, the d_{001} distance turns out to be 19.0 Å whereas in the conventionally prepared sample it is 19.7 Å.

De Andrés et al. [26] report a very complete characterization of Al-pillared montmorillonite prepared either by the conventional method or by microwave irradiation during the intercalation step for 2, 10, 18, or 20 min. The same samples are, then, thermally treated at 450 °C. This study is complementary of the previous one [25], as it performs thermal gravimetry analysis–differential thermal analysis (TGA–DTA), impedance spectroscopy, ²⁷Al magic angle spinning nuclear magnetic resonance (MAS NMR), and intercalative adsorption of Methylene Blue (MB) and concludes that the irradiated samples are intermediate between non-treated-intercalated samples and conventionally pillared samples. It appears that at least a fraction of the interlayer Al-polycations remain hydroxylated and linked to some

coordinated water molecules. If Al_2O_3 pillars have to be anchored to the silicate layers, these microwaved materials need an additional thermal treatment to achieve the usual properties inherent to conventional aluminum-pillared montmorillonite. The proton availability, in the only microwaved materials, should be useful to catalyze acidic reactions. Their good thermal stability also supports this type of application.

Nevertheless, prolonged irradiation produces structural and textural damages. Basal spacing, specific surface area, and pore volume are of the same order of magnitude as those of conventional aluminum-pillared montmorillonite. The interlayer distances ($d_{001} = 17.2\text{--}16.9 \text{ \AA}$) decrease as the microwave irradiation time increases. Specific surface areas (BET, N_2) are in the $300\text{--}400 \text{ m}^2/\text{g}$ range, with micropore volume in the order of $0.15 \text{ cm}^3/\text{g}$, which is close to values of conventional aluminum-pillared clays although they decrease from 399 to $296 \text{ m}^2/\text{g}$ as the microwave irradiation time increases from 10 to 20 min.

A special mention has to be made to boehmite sol-intercalated smectites [21]. The intercalated smectite was dried in an oven at $60 \text{ }^\circ\text{C}$ over a period of 24 h and also in a microwave oven of 2.45 GHz frequency and 600 W power over a range of 3–15 min. Both kinds of samples have identical thermal and electrical properties. However, the microwave-dried samples have a distinctly higher surface area of $120 \text{ m}^2/\text{g}$, stable up to $650 \text{ }^\circ\text{C}$ with a marginal reduction to $116 \text{ m}^2/\text{g}$ compared with $94 \text{ m}^2/\text{g}$ for the oven-dried sample. Similarly, there is a clear difference in the morphological features of the two kinds of samples, the air-dried sample having a close-packed structure while the microwave ones were delaminated and porous.

1.3.1.2 Zirconia-Pillared Montmorillonite

If the mixture of clay and zirconium solution is irradiated (intercalation step) for 5, 10, 20, and 30 min, maintaining the ratio of zirconium to clay constant and equal to 2 mmol/g, the interlayer distances, determined by X-ray diffraction, turn out to be 19 \AA [27]. This value can be compared to the 12.4 \AA of the initial montmorillonite, showing that all samples are intercalated. Nevertheless, the intensity and broadness of the 001 diffraction peaks show an inhomogeneous stacking of the clay layers, typical of the zirconium-pillared compounds [28]. Indeed, the expected zirconium species, present among others, in solution is the hydroxocation $[\text{Zr}_4(\text{OH})_8(\text{H}_2\text{O})_{16}]^{8+}$, which rapidly polymerizes to form other species [29]. Then, the montmorillonites are expected to be intercalated with several zirconium species possessing different sizes causing the irregular stacking of the clay layers. There is a slight effect of the irradiation time on the pillaring of the montmorillonite; the 001 and 002 peaks, in X-ray diffraction patterns, are slightly more intense for samples irradiated for 10–30 min than those microwaved for 5 min. The conventionally prepared sample presented 001 peaks similar to those of the 5-min irradiated sample. Hence, a better pillaring is obtained if samples are microwave-irradiated.

When the Zr/clay ratio is increased to 5 mmol/g, the 001 diffraction peak turns out to be well-defined only for the samples intercalated by microwave irradiation for 10–30 min. The interlayer distances are about 19.2 Å. The amount of zirconium used in the syntheses does not alter significantly the structural parameters. Independently of the amount of zirconium, the intercalation method or the intercalation time, the surface areas are ca. 160 m²/g in the samples pillared by microwave irradiation. These surface area values are similar to those obtained with the corresponding non-irradiated samples. The comparison of the ammonia thermodesorption curves shows that all curves are similar showing that acidity features are independent of the synthesis method as well as the irradiation time for 2 or 5 mmol of zirconium/g of clay. As the ammonia desorption is carried out with water and hydroxyl radicals, not only the acidity but also the hydration degree is the same [27].

1.3.1.3 Titania-Pillared Montmorillonite

The intercalation of titanium in montmorillonite, in presence of microwave irradiation, provides a 001 distance from 14.0 to 22.0 Å and surface area of 281 m²/g. The advantages of irradiation, in this case, are, again, on the one hand, a significant reduction of the aging time (about 100 times, if compared to the conventional method) and, on the other, solid concentrations in the pillaring suspension are increased up to 20 times [30]. Furthermore, a higher stability of the layer stacking was verified: contact time between clay and acid pillaring solution is short and, therefore, the clay is not dealuminated.

Microwave irradiation for 15 min during the calcination step has been shown to produce Ti-montmorillonite which, used as photocatalyst, is active in the remotion of 4-chlorophenol in water and methanol in air. Microwave-calcined samples led to an activity that was less than TiO₂ P-25 for 4-chlorophenol removal in water but higher for methanol removal in air. This behavior might result from a higher surface area of pillared TiO₂ and perhaps a different distribution of pores. TiO₂-pillared montmorillonite may include a smaller density of irregularities prone to behave as recombination centers of the photo-produced charges [7].

When the sample is irradiated for 30 min in a multi-mode domestic microwave oven operated at 700 W with 2.45 GHz, and then calcined at 400 °C, no 001 distance appears in the X-ray diffraction pattern. Therefore, in those conditions the pillared montmorillonite does not present a sufficiently ordered and oriented layer structure [23].

However, if titanium-pillared clays are prepared conventionally [31], either from TiCl₄ or Ti(OC₃H₇)₄ precursors, the 001 distance is 19.3–19.9 Å and the surface area turns out to be 229–277 m²/g [32, 33]. In fact, the 001 distance depends on the H⁺/Ti ratio as d_{001} , for a H⁺/Ti ratio of 1.2, is 14.1 Å but it is 15.9 and 26.2 Å if the ratio is 0.24. The clay prefers to be exchanged with H⁺.

Still, it has been reported that, after conventional intercalation, samples may not exhibit the 001 basal reflection. In such cases, a mixture of pillared structure and partially delaminated structure has been proposed [23, 34].

1.3.1.4 Multimetallic-Pillared Montmorillonite

Ti/Zr-pillared bentonites have been prepared using microwave irradiation in the calcination step. The sharp (001) peak of the Ti/Zr-pillared montmorillonites is found to be at $2\theta = 4.2^\circ$ ($d = 24 \text{ \AA}$) due to polycationic species of titanium and zirconium. Note that the Na-montmorillonite shows a 001 peak at $2\theta = 10.2^\circ$ ($d = 10 \text{ \AA}$). Microwave irradiation for 15 min, with a commercial oven operating at 2.45 GHz and at a power level up to 300 W, improves the photocatalytic activities of the samples in the removal of 4-chlorophenol and dichloroacetic acid in water [20]. The higher activity of microwave irradiation-calcined samples might result from a higher surface area and a different pore distribution. Indeed, a solid sample is uniformly heated in the bulk and on the surface when submitted to microwave irradiation. Consequently, the microwave drying is supposed to facilitate the transport of water molecules toward the surface, unlike a conventional heating where the heat is transferred from the surface to the bulk.

Unfortunately it seems that not many studies on complex pillaring under microwave irradiation have been published, although, many complex pillars have been synthesized conventionally. They may be constituted by two metals as: aluminum and lanthanides [35], aluminum and silicon [36, 37], or silicon and zirconium [38].

Large-pore montmorillonites pillared with aluminum–lanthanum complexes have been synthesized in presence of microwave irradiation in the pillaring solution preparation at different times and in the intercalation step for 10 min [39, 40]. The microwave treatment of the intercalation solution with a molar ratio of Al/La of 5 for 1, 3, and 5 h results in pillared clays with specific areas of 182, 226, and 245 m²/g, respectively. The interlayer distances were ca. 26.0 Å, much larger than those obtained with Keggin-type aluminum pillars (ca. 18 Å). When the Al/La ratio increased to 30 the surface area decreased to 168 m²/g and the interlayer distance turned out to be 24.7 Å. These results show that microwave irradiation applied to prepare pillaring solutions can reduce the time from 120 h by the conventional method to 3 or 5 h. The intercalation time is reduced from 18 h (conventional) [41–44] to 10 min with microwaves.

Pillars constituted by three different metals have also been reported: aluminum, zirconium, and cerium [45] or aluminum, iron, and cerium [46] into montmorillonite layers. The effect of microwave irradiation has not been established on those materials. New compounds should appear as association of metals in the pillars is expected to be different due to the strong energetic effect of microwaves.

An interesting proposition is to prepare a monometallic-pillared montmorillonite and to use it as support for other metals, for instance, a titania-pillared clay has been vanadia doped to use it in the epoxidation of allylic alcohol (*E*)-2-hexen-1-ol [33]. This catalyst was found to be more active than Ti-pillared clay for the epoxidation.

Supported vanadium-containing catalysts have been prepared by impregnation of Al-pillared clays with NaVO₃ precursor aqueous solutions. A montmorillonite and a saponite pillared with Al₁₃ Keggin polycations were used as supports [47]. Again, the microwave irradiation effect on those materials has to be determined.

1.3.1.5 Remarks

These studies show that an irradiation time of ca. 10–30 min provides the most ordered materials. Higher irradiation times only lead to disordered clays with structural and textural damages. Acidity is independent of irradiation time. The microwave irradiation guarantees short contact times between clay and the acid-pillaring solution, therefore the clay is not dealuminated. Furthermore, microwave drying is assumed to favor the water molecules transport toward surface unlike a conventional heating where heating is transported from the surface to the bulk. Such features may explain the differences in pillar distribution and catalytic performance of the microwave-irradiated and conventional samples.

1.3.2 Clay to Water Ratio

1.3.2.1 Alumina-Pillared Montmorillonite

It is known that the Al/clay ratio has a significant effect on the accessibility properties in Al-pillared clays. If highly concentrated clay suspensions (10–50 wt% of clay in water instead of the usual 0.5 wt%) is used, and the irradiation is maintained for 7 min after the clay is mixed with chlorhydrol (aluminum polyoxocation), the inter-layer distances turn out to be again 19.0 Å and the large surfaces are reproduced (335 m²/g) [17]. This result is most important as, without microwave irradiation, intercalation is very hard and the specific surface is low. Molina et al. [48] have used a dialysis technique for intercalation and washings to prepare alumina-pillared montmorillonite from a 40-wt% clay slurry. They observed that the intercalation occurs mainly during the washing step, where, indeed, the system is highly diluted.

A different approach was followed by Perez-Zurita et al. [49], who report the synthesis of Al-PILC assisted by ultrasound. They managed to reduce the intercalation time and the amount of synthesis water. The clay to water content was in this case 30% (w/w) clay in water and the amount of water was reduced by 60% if compared to conventional preparations. The obtained specific surface areas were comprised between ca. 100 and 200 m²/g depending on the ratio Al/g of clay. The conventionally prepared clay presented a 001 interplanar distance of 18 Å whereas the ultrasound-intercalated clays show distances comprised between 16 and 19 Å. The main effect of ultrasonic radiation is to reduce the size of the clay grain and, as a consequence, the Al precursor diffusion, toward the core of the particle, is improved.

1.3.2.2 Iron oxide-Pillared Montmorillonite

The preparation procedure of iron oxide-pillared montmorillonite has to be explained in detail, in this case, as the sample was irradiated 3 times [50]. A slurry

composed of 1 g of montmorillonite in 100 ml of water was added to the solution already irradiated for 10 min (15 mmol of iron per g of clay) and placed in a microwave oven for 10 min at low power. Distilled water was added to the resulting mixture which was placed again in the microwave oven for further irradiation for 10 min.

One of the main advantages of irradiation, which is the use of highly concentrated clay suspensions and solutions, is not explored in the Berry et al. (1994) work [50]. The water to clay ratio in iron oxide-pillared montmorillonite is 1% while in the previous alumina-pillared montmorillonite it is 10–50%. Still, iron oxide-pillared montmorillonite under those conditions can be prepared in less than 1 h by a process involving microwave heating. The iron oxide pillars are progressively reduced in hydrogen at temperatures between 300 and 600 °C. The metallic iron formed at 600 °C is unaffected by exposure to oxygen at room temperature and partially oxidized when heated in oxygen at 300 °C.

1.3.2.3 Remarks

Concentration of clay suspensions may be increased with the use of microwave irradiation. Highly concentrated clay suspensions, 10–50%, instead of the conventional 0.5–1%, irradiated for 7 min, provide the required dispersion of the clay. Such result is determinant for any large-scale preparation of intercalated clays as the amount of water is strikingly reduced.

1.3.3 Metal to Clay Ratio

1.3.3.1 Titanium-Pillared Clays

If conditions to pillar with titanium are compared to those of Al pillaring or Zr pillaring, the performance of the microwave irradiation method is clear [23]. In non-irradiated preparations, titanium pillaring is most difficult. Instead, if the samples are prepared in the presence of microwave irradiation, the pillaring is easily achieved, and the pillars turn out to be preferentially anatase phase. This point is most important as these materials exhibited good photocatalytic degradation performance of Methyl Orange. In the same experimental conditions, the non-irradiated samples present a ratio of anatase to rutile three times less than the irradiated preparation.

1.3.3.2 Zirconium-Pillared Montmorillonite

The synthesis, at different zirconia/clay ratios, of zirconia-pillared montmorillonite in presence of microwave irradiation has been reported [27]. If the metal/clay ratio is 2 mmol/g of clay the montmorillonite is expanded to a d_{001} of 19 Å. If the ratio is 5 mmol/g of clay, d_{001} turns out to be 19.2 Å. Therefore, the amount

of zirconium does not alter significantly the structural parameters. All samples, microwave-irradiated or not, present the same surface areas and acidity features. As well, if the samples are sonicated [51], the structural features are independent of the metal/clay ratio (0.2–1.3 mmol Zr/g of clay) but the specific surface area evolves from 272 to 214 m²/g.

The expected zirconium species present in solution is the hydroxocation [Zr₄(OH)₈(H₂O)₁₆]⁸⁺. The main pillaring species appear to be nanorods composed of several Zr₄ tetramers. The basic features of the tetramer structure are preserved in zirconia nanoparticles fixed between aluminosilicate layers in pillared clays. In calcined samples, those nanoparticles contain only bridging hydroxyls and/or oxygen anions responsible for bonding within pillars and between pillars and clay sheets [52].

1.3.3.3 Remarks

The metal–clay interaction seems to be specific of each metal although not enough work has been done in this direction with microwave irradiation. In titania-pillared montmorillonite, microwave irradiation promotes a higher anatase formation than the conventional preparations. Instead, zirconium-pillared samples in presence or not of microwave irradiation (or sonication) are similar to those prepared conventionally as acidity and interlamellar distance remain the same. The amount of intercalated metal does not alter those results, the interlamellar distance (19 Å) is the same from 2 to 5 mmol/g of clay.

1.3.4 Ultrasound Versus Microwave Irradiation

Although this work is centered in microwave irradiation, it is illustrative to compare the effect of microwave irradiation to other wavelengths as ultrasound or gamma irradiations, Table 1.1. The interest of sonication is exemplified by the following result. Aluminum oligomers may be introduced into Ca²⁺-montmorillonite using ultrasonics within 20 min at ambient temperature [53]. In the conventionally prepared pillared clay the lamellar structure is lost at around 700 °C whereas the sonication for 20 min results in a pillared clay stable up to 800 °C. The observed higher thermal stability can be explained on the basis of uniform distribution of the

Table 1.1 Comparison of microwave, ultrasonic, and gamma irradiation features

| Radiation type | Wavelength | Typical frequency (MHz) | Chemical bond energy (kcal/mol) |
|------------------|------------|-------------------------|---------------------------------|
| Gamma rays | <10 pm | 3.0×10^{14} | 120 |
| Microwaves | 1 mm–1 m | 2,450 | 4.8 |
| Ultrasonic waves | ca. 1.5 mm | 0.002 | – |

pillars within the layers. Ultrasonication for 20 min results in an optimum d -spacing and a very high surface area with an optimum micropore volume, 19.2 Å, 281 m²/g, 0.11 cm³/g, respectively.

The intercalation time and the water amount (<60%) are significantly reduced with ultrasonic irradiation as stated by Pérez-Zurita et al. [49]. The improvement of the Al pillar distribution is attributed to a smaller particle size, i.e., a better delamination of the aluminosilicate layers due to sonication, which may increase the space available between the layers, thus enhancing the extent of intercalation and reducing considerably the reaction time [54]. Furthermore, it has been claimed that through sonication pillars are well distributed without any non-pillared portion of the clay [55]. Strong acid sites and sufficient gallery height of Zr-PILC seem to promote the activity in alkylation of benzene with long-chain olefins to produce dialkylbenzenes.

Microwave and ultrasound irradiation effects have been combined to obtain Zr-pillared clays [24]. The pillaring solution is irradiated with microwaves (5, 10, 20, or 30 min), then, the clay is intercalated in presence of ultrasounds (5, 10, 20, 30, or 40 min). The resulting materials have been tested under microwave irradiation in the acylation of various primary, secondary, tertiary, and benzylic alcohols and mono-acylation of 1, n -diols with acetic anhydride under solventless conditions. The catalysts are reactivated using again microwave irradiation. The advantages were mainly in operational simplicity, recyclability, and selectivity. The better conditions were obtained with a catalyst prepared with an ultrasonication of 30 min. Still, if the sonication is performed during the preparation of various biologically active dihydropyrimidinones, the reaction takes longer time and the product yield is lower [5].

Instead, if the irradiation is gamma, no change attributable to irradiation is observed, only a small variation in the water content is noted but it is not systematic. The effect of heavy doses (up to 200 Mrad) on the short-range structural organization in montmorillonite has been studied using infrared spectroscopy and solid-state high-resolution²⁷Al and ²⁹Si nuclear magnetic resonance [56].

When perfect and imperfect kaolinites, palygorskite, montmorillonite, muscovite, synthetic gibbsite, or brucite are exposed to high doses of γ -irradiation (10⁵, 10⁶, 10⁷, 3 × 10⁷ Gy) the Al³⁺ leaching from kaolinite increases, but that of Si⁴⁺ decreases; for montmorillonite and palygorskite the other way round. The irradiation dose leads to different types of defects which may be correlated with the increase of specific surface and solubility [57].

These results may be understood from the main principles of wave interaction with matter. Microwave effects in organic synthesis have been tentatively rationalized [58], whereas no clear mechanisms have been proposed for inorganic reactions. Still, details concerning the application of microwaves to chemical reactions have been proposed [59]. Two mechanisms have been advanced. Many researchers think that the observed acceleration of the reaction rates could be due to the different modes of transferring heat to the reagents and solvents. Others on the contrary suggest that absorption of microwave radiation has some specific activating (non-thermal) effect on the reagent molecules. Actually, the acceleration of reactions

by microwave exposure results from material–wave interactions leading to thermal effects (which may be easily estimated by temperature measurements) and specific (non-purely thermal) effects.

Non purely-thermal effects can be envisaged to have multiple origins. These effects can be rationalized through the Arrhenius law, $k = A \exp(-\Delta G^*/RT)$, and can result from modifications in each of the terms in this equation. Decrease in activation energy ΔG^* is for sure a main effect.

Gamma irradiation is also an electromagnetic wave whose wavelength is much shorter (less than 10 pm) but the frequency is much higher (3.0×10^{14} MHz) and thus, it does not heat the samples nor promotes molecular diffusion. Instead, due to the high energy of the waves, it is able to dissociate molecules. It has been used to change white topaz into blue topaz.

In this context, the comparison with sonication (ultrasound irradiation) is interesting as sonication only promotes heat transfer combined with a pressure increase. If ultrasonic energy at high power, more than $1/3 \text{ W/cm}^2$ for water at room temperature, is applied to a liquid, cavitation takes place [60]. These conditions are very short-lived although they have been used to synthesize diamonds [61]. They may result in the generation of highly reactive species including hydroxyl, hydrogen, and hydroperoxyl radicals and hydrogen peroxide. Such radicals may initiate or promote many reduction–oxidation reactions. Reactions with organic and inorganic substrates are, then, fast and may reach the diffusion-controlled rate [62].

Assuming adiabatic bubble collapse, the maximum temperatures and pressures within the collapsed cavitation bubbles are predicted by Noltingk and Neppiras from approximate solutions of Rayleigh–Plesset equations [63]. Note that frequency has a significant effect on cavitation because it alters the critical size of the cavitation bubble. At very high frequencies, the cavitation effect is reduced. Lower frequency ultrasound produces more violent cavitation, leading to higher localized temperatures and pressures. Last but not least, there are two extremes with respect to power: the threshold power which must be surpassed and the optimum power beyond which further power increases have no effect [64].

1.3.4.1 Remarks

As already mentioned, the interaction of ultrasound waves or microwaves with matter follows two mechanisms which may both result in an acceleration of chemical reactions. Microwaves are electromagnetic waves with wavelengths ranging from 1 mm to 1 m, or frequencies between 0.3 and 300 GHz, whereas ultrasound waves (20–200 kHz) are cyclic sound pressure waves with a wavelength of ca. 1.5 mm. Thus, the interaction with matter is definitely different and they should be used depending on the required result. If the material has to be altered at the atomic level, gamma irradiation is recommended.

Microwave interaction with materials leads to thermal and specific effects. Sonication instead promotes heat transfer combined with a pressure increase.

1.4 Other Clays

1.4.1 Clay Synthesis

A promising method to synthesize clays using microwave irradiation has been reported. Fast microwave synthesis of hectorite has been obtained by Vicente et al. [65], according to the method reported in which brucite sheets act as crystallization nuclei of hectorite, as proposed by Granquist and Pollack (1959) [66]. A slurry, containing the brucite seeds freshly prepared, lithium fluoride, and silica, was stirred for 1 h. The resulting mixture was treated in a microwave equipment at 100 °C for 4 and 8 h or at 120 °C for 4, 8, or 16 h. Higher proportions of hectorite with higher crystallinity were achieved at longer aging time, higher temperature, and by using a more crystalline brucite. However, the highest purity was 60%. Note that the conventional method provides a 40% hectorite mixture. In summary, the hydrothermal microwave treatment provides a faster synthesis of hectorites, more than 10 times. However, such synthesis has to be improved as no successful pillaring would be achieved with low purity clays.

1.4.2 Aluminum-Intercalated Samples

Other clays, not only montmorillonite, have been pillared. Microwave irradiation has been found to enhance the intercalation of aluminum complexes into rectorite due to the promotion of ion exchange during synthesis. Rectorite has a 2:1 layer structure in a regularly interstratified clay mineral of dioctahedral mica layer and dioctahedral smectite layers in a 1:1 ratio. This clay consists of alternate pairs of mica-like (non-expandable) and smectite-like layer (expandable). Mica-like layers increase the thermal stability of rectorite; smectite-like layers determine its pillaring possibility. Thus, aluminum-pillared rectorites should be resistant cracking catalysts. They have been already synthesized using microwave irradiation [67].

1.4.3 Titania-Pillared Clays

Conventionally, titanium-pillared clays using montmorillonite, saponite, and rectorite hosts have been prepared from TiCl_4 -ethanol solutions. Of course, the amount of Ti incorporated is related to the cation-exchange capacity of the host. Saponite has the highest acidity, and this is reflected in the highest conversion for cumene cracking. In the case of pentanol dehydration, however, the highest activity is seen for the rectorite sample, despite its apparent lower acidity. Similar effects have been reported previously for this reaction with alumina-pillared clays. The thermal stability decreases from rectorite through montmorillonite to saponite [32].

Microwave irradiation has been used in the sol-gel synthesis of the small titanium nanoparticles which were supported on laponite [68]. The photocatalytic

activity improves by increasing the Ti/clay ratio as a greater number of active anatase sites are provided and also by the use of hydrothermal treatment which enhanced the anatase crystallinity.

1.4.4 Chromia and Tin Oxide-Pillared Montmorillonites and Laponites

Tin oxide-pillared laponite has been formed under ambient conditions from aryltin precursors using microwave heating [69]. The pillaring was achieved via neutral precursors rather than by sacrificial reaction of the exchanged cation. The intercalation/pillaring reactions are much more rapid (5 min) when carried out in containers in a simple domestic microwave oven. Combined ^{119}Sn Mössbauer and X-ray photoelectron spectroscopic studies suggest that, in the microwave experiments, Ph_3SnCl has a higher initial affinity for the clay surface than $(\text{Ph}_3\text{Sn})_2\text{O}$ but that the chloride undergoes hydrolysis on the surface once sorbed. Evidence for the considerable mobility of Mg^{2+} within the laponite lattice during microwave heating is provided.

Gyftopoulou et al. [6] report the preparation of chromia and tin oxide-pillared montmorillonites and laponites using both conventional and microwave-assisted methods. For the microwaved tin oxide-pillared montmorillonite, a water solution of ammonium hexachlorostannate was mixed with a bentonite suspension and irradiated at 100 W for 15 min at 100 °C. The authors find that the microwave method can be considered successful for the synthesis of tin oxide-pillared montmorillonite as, by XRD measurements, it is shown that the sample presents the same trend as the conventionally prepared ones. For the microwaved tin oxide-pillared laponite, a sodium-exchanged laponite and triphenyltin chloride were mixed with dry ethanol and irradiated for 5 min at 100 W. In this case X-ray powder diffraction is not a suitable method for characterizing pillared laponites due to the lack of first-order reflection. It is replaced by X-ray photoelectron spectroscopy, which shows that in the case of tin oxide-pillared laponites the amount of tin varies among the different preparations although no clear trend is observed relating it with the preparation conditions.

For the microwaved chromia-pillared montmorillonites two sets of experiments were performed: (1) the intermixed solution of chromium nitrate and sodium carbonate was added slowly to the clay suspension and then microwave-irradiated at different power, time, and temperature; (2) the intermixed solution of chromium nitrate and sodium carbonate was microwave-irradiated at 150 W and 105 °C for 15 min. Then, the microwave-treated solution was mixed with the clay suspension and stirred for 1.5 h. The authors [6] find that with microwave irradiation a considerably faster preparation, possibly with highly concentrated clay suspension and pillaring solutions, can be achieved, leading to large-scale production of pillared clays. The basal spacing of 20 Å is not as high as that following the conventional method (27 Å) by Pinnavaia et al. [70], but it is in agreement with other reports and confirms some pillaring [71].

The prepared PILCs were employed as catalysts in the hydrocracking of coal-derived liquids in a conventional microbomb reactor exhibiting high-quality performance and remaining active after 4 h utilization regardless of high coke deposition [6]. When reused, an increase in the total conversion was shown. Although, a range of catalysts with different structural properties depending on texture, morphology, way of preparation, nature of clay catalyst, nature of active metal, etc., were prepared, the selected hydrocracking reaction does not show any particular sensitivity to these factors.

1.4.5 Saponite Pillared with Fe-Organometallic by Microwave and Ultrasound Irradiation

Natural Na-saponite was intercalated with an iron complex: $[\text{Fe}_8(\mu_3\text{-O})_2(\mu_2\text{-OH})_{12}(1,4,7\text{-triazacyclononane})_6]^{7+}$, which behaves as a single molecule magnet at low temperature, by the conventional method and by microwave or ultrasound irradiation [72]. An interlayer distance of 15.6 Å is found for the irradiated samples and 13.7 Å for the sample prepared conventionally. Since the Fe-complex size is ca. 10 Å, only the microwave or ultrasound irradiation promotes the Fe-complex intercalation. This complex conserves the structure of the polycation inorganic core: connectivity seems to be maintained, while the polycations must be somewhat flattened by strain due to intercalation. Magnetization experiments appear compatible with a conservation of the polycation nuclearity.

1.4.6 Pillared Anionic Clays

1.4.6.1 Polyvanadate-Intercalated Hydrotalcites

Hydrotalcites are anionic clays, whose chemical formula is $[\text{M}^{2+}_{1-x}\text{M}^{3+}_x(\text{OH})_2](\text{A}^{m-})_{x/m}\cdot n\text{H}_2\text{O}$, where M^{2+} may be replaced by three-valent cations, M^{3+} , which produce positively charged layers, as described in a previous chapter. Hydrotalcite may be synthesized by precipitation or through the sol-gel method among others. They may be prepared in presence of ultrasound or microwave irradiation. Those conditions determine the properties of hydrotalcite-like compounds [73–78].

Hydrotalcites have been intercalated with decavanadate polyoxo complexes in presence of microwave irradiation during the intercalation process as well as during the hydrotalcite crystallization step. The d_{003} distances of the intercalated samples are 11.8 or 7.8 Å depending on irradiation time, 1 or 5 min, respectively. The specific surface areas turn out to be 52 and 60 m²/g for the 1 and 5 min irradiated samples. The interlayer distance of the non-pillared hydrotalcite is 7.7 Å. These compounds were tested in the aldolic condensation of acetone. As expected, the sample irradiated for 1 min, presenting a higher layer expansion, is the most active [79].

1.4.6.2 PO_4^{3-} and $P_2O_7^{4-}$ -Intercalated Hydrotalcites

Zhang et al. [80] report the intercalation of PO_4^{3-} and $P_2O_7^{4-}$ species in carbonated Mg–Al- or Zn–Al-hydrotalcites by direct anion-exchange reaction in presence of microwave irradiation at 90°C for 10 min. By infrared spectroscopy it is shown that the CO_3^{2-} band of the original hydrotalcite disappears in the intercalated materials and the characteristic bands of the PO_4^{3-} or $P_2O_7^{4-}$ species appear, confirming intercalation. The X-ray diffraction patterns of the PO_4^{3-} or $P_2O_7^{4-}$ -intercalated Mg–Al-hydrotalcites show broader peaks compared with those of the carbonated Mg–Al-hydrotalcite. In the case of Zn–Al-hydrotalcites the 003 peak at $2\theta = 11.6^\circ$ becomes less intense by intercalation with PO_4^{3-} and even disappears with $P_2O_7^{4-}$ interlayered. This peak broadening has been assigned to a disturbance in the structure due to the pillaring with PO_4^{3-} or $P_2O_7^{4-}$ species. The authors conclude that the microwave method can destroy the acting force between lamellar structures so that phosphate or pyrophosphate ions can easily exchange carbonate ions. Therefore, the microwave method cannot only make the exchange reaction possible but also shorten the interaction time dramatically to obtain crystalline products.

1.4.6.3 PET–Hydrotalcite Nanocomposites

The hydrotalcite has been organically modified using dodecyl sulfate as the interlamellar anion, to overcome the lack of compatibility between the polymer and hydrotalcites containing purely inorganic anions, such as carbonate and nitrate. Then, the polyethylene terephthalate (PET) –hydrotalcite nanocomposites have been prepared as follows. The PET precursors were microwave-irradiated while the hydrotalcite is dispersed in an ultrasonic bath [81]. The authors show that in situ polymerization under microwave irradiation constitutes an alternative method for preparing PET–hydrotalcite nanocomposites. The preparation time is considerably reduced and the inorganic filler results well dispersed and exfoliated in the polymer matrix. The nanocomposites obtained are thermally more stable than original PET.

1.4.6.4 Remarks

The intercalation of other clays than montmorillonite in presence of microwave or ultrasound irradiation has been reported. The thermal stability of the intercalated material seems to increase from saponite, through montmorillonite to rectorite. An interesting result is that aluminum-intercalated rectorite can be a resistant-cracking catalyst and that only microwave or ultrasound irradiations promote the Fe-complex interaction with saponite. Note that anionic clays have been intercalated in presence of microwave irradiation. The main advantages of irradiation are those already reported: faster preparation, easier preparation, and most important the use of concentrated solutions. Furthermore, irradiation improves thermal stability.