

## Review

## Non-cordierite clay-based structured materials for environmental applications

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## ABSTRACT

The applications of clay-based structured materials, excluding cordierites, for environmental protection are examined. In particular, their use in the abatement of some of the main hazardous species in polluted emissions such as nitrogen oxides, carbon monoxide, volatile organic compounds and heavy metals is discussed. A distinction is made between adsorption and catalytic processes. In addition, a general overview of the methods and general principles followed to prepare structured materials from clays is also given. Special attention is paid to those employed to obtain honeycomb monoliths and foams.

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## Contents

1. Introduction.....	9
2. Preparation methods.....	10
2.1. Extrusion.....	10
2.2. Foams.....	12
2.3. Others.....	12
3. Environmental applications.....	13
3.1. Adsorption.....	13
3.2. Catalysis.....	14
4. Conclusions.....	16
Acknowledgements.....	16
References.....	16

## 1. Introduction

The relationship between clays, health and environment is as ancient as it is diverse [1]. For a very long time, these materials have been known to be beneficial to human health due to their characteristic surface properties, such as large specific surface area compared with other natural resources, their layer charge, and swelling capacity. As a result, they have been extensively employed as active principles, or as excipients in pharmaceutical formulations, spas, and aesthetic medicine. Being good adsorbents and muco-stabilizers, clay minerals are also useful as drugs in the treatment of intestinal disorders. Furthermore, as recognition of the

need to develop technologies for pollution control grew worldwide, new applications were found for them in this field, because of their large propensity for adsorbing and immobilizing extraneous species. Table 1 summarizes the most classic applications reported for clays in environmental protection, which are mainly, although not exclusively, related to polluted soil and wastewater treatments. Nowadays, due to their abundance and low cost, clays are also used in atmospheric pollution control. In this sense, an example of their ever-growing versatility is that some clays have recently been proposed as good candidates for CO<sub>2</sub> sequestration to reduce the greenhouse effect [2].

One of the most innovative elements that have appeared in recent decades in the context of technologies for treating polluted effluents before their emission to the environment are the so-called structured materials [3]. This is a new family of reaction systems whose open and ordered structure avoids the main

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**Table 1**  
Applications of clays for environmental protection.

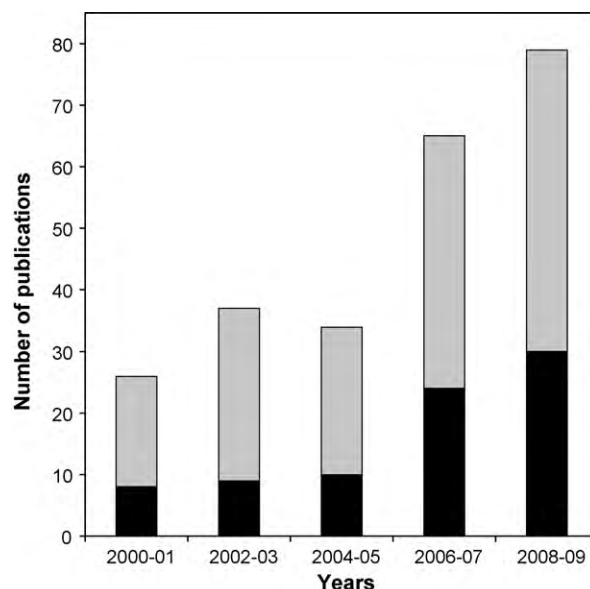
Control of heavy metal cations and simple cations ( $\text{Cu}^{2+}$ , $\text{Pb}^{2+}$ , $\text{Zn}^{2+}$ , $\text{Ca}^{2+}$ , $\text{Cd}^{2+}$ , $\text{Mg}^{2+}$ , ...)
Control of organic and biological cations (pesticides, waste proteins from food processing, ...)
Control of non-ionic organic compounds (oils, greases, ...)
Control of anions (phosphates, iodides, nitrates, chromates, ...)
Control of turbidity and residual treatment chemicals (natural organic matter, surfactants, polyelectrolytes, ...)
Carriers of pesticides (to reduce their leaching, photodegradation and volatilization)
Liners in waste disposals (encapsulation)
Barriers in nuclear waste management

problems of conventional packed-bed reactors, which are the random and structural maldistributions that originate from the looser packing of particles near the reactor walls. This results in a tendency to bypass the core of the bed, even if the initial distribution of fluid(s) is uniform, drastically altering its residence time from the design value.

Among structured materials, honeycomb monoliths are by far the most popular adopted form, the literature devoted to them being really vast [4–7]. Consisting of continuous unitary structures that contain a large number of straight, identical, parallel channels, equally accessible to the contact with the flow, they have been found to be effective in the cleaning of exhaust gases from stationary and mobile sources. This is because they offer very low pressure drop, high resistance to plugging, and a high geometric area per unit volume, which make them very useful in solid-catalyzed gas phase chemical reactions [6]. They are extensively used in automotive and stationary emission control, but they are also increasingly used in many other applications, such as in chemical processing industries, catalytic combustion, pollution abatement of volatile organic chemicals, and oxidation of carbon monoxide and unburned hydrocarbons, among others.

There is no doubt that over many years honeycomb monoliths have become the standard catalyst shape in most applications of environmental catalysis. In addition, more recently, the application of monolithic catalysts has been proposed as an intensification method in some classical processes of the industrial chemistry. In fact, the adoption of structured catalysts with highly conductive supports makes it possible to remove (in the case of exothermic processes) or supply (in the case of endothermic processes) the heat of reaction easily, allowing these processes to be carried out on an industrial scale with small temperature gradients both in the axial and in the radial direction, with specific productivity similar to or higher than conventional reactors [8]. Nowadays, the interest of the scientific community in this kind of materials is so evident that an international conference specifically focused on structured catalysts and reactors is held on a regular basis.

From the very beginning of their use in technological applications, their rheological properties have made clays and clay minerals ideal raw materials for preparing structured supports and catalysts [9–11] being a better alternative to metallic ones. However, most of the work performed in this regard has dealt with the production of the very well-known synthetic ceramic called “cordierite” [4,5,12]. Compositions based on this material,  $2\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$ , possess a unique combination of several critical characteristics: (a) thermal shock resistance due to a low thermal expansion coefficient; (b) porosity and pore size distribution suitable for ease of washcoat application and good washcoat adherence; (c) sufficient refractoriness because the melting point exceeds  $1450^\circ\text{C}$ ; (d) sufficient strength for survival in an automotive exhaust environment; and (e) compatibility with washcoat and catalysts. Table 2 and Fig. 1 illustrate the great and increasing attention this material has received, not only from scientists, but also



**Fig. 1.** Evolution of the number of patents (dark) in relation to the total of publications (light) dealing with cordierite synthesis from clays in the last ten years.

from industry. In particular, cordierites are the source of inspiration for patents.

Nevertheless, from the processing prospective, cordierite substrates are clay-based structured materials with a high energy demand as they are the result of firing previously moulded ceramic pastes at very high temperatures (usually above  $1300^\circ\text{C}$ ). Moreover, these pastes are basically prepared from a mixture of talc with alumina to which clays are just added to favour the extrusion process. In a similar way, there are many studies in which clays, although part of a structured support, are not the majority component but mere binders to shape other materials into ceramic bodies. The list of these materials is long and includes carbon, mainly activated [13,14] but also in the form of coals [15], carbon black [16] and even carbon fibres [17],  $\text{TiO}_2$  [18–21],  $\text{Al}_2\text{O}_3$  [18,22], zeolites [23,24], mullite [25],  $\text{SiC}$  [26],  $\text{Al}_2\text{O}_3\text{--SiO}_2$  [19,27],  $\text{ZrSiO}_4$  [28],  $\text{FeTiO}_3$  [29],  $\text{B}_2\text{O}_3$  [30],  $\text{Fe}_2\text{O}_3\text{--Cr}_2\text{O}_3$  [31],  $\text{Al}_2\text{TiO}_5$  [32],  $\text{LiAlSi}_4\text{O}_{10}$  [33], etc.

The purpose of this review is to show a broader reality that extends beyond the limits of these materials and, in general, of cordierites. We present a selection of cases of clay-based structured materials in which clays are the main component, both from the compositional and functional viewpoint. First, the most common procedures to prepare them are briefly described. Then their application in environmental uses is discussed, putting the emphasis on the key role played by the clayey fraction of the structure.

## 2. Preparation methods

### 2.1. Extrusion

The plastic properties of clays make them very appropriate materials for processing through extrusion, i.e. to elaborate pastes that can be first forced in a press to pass through a die to acquire a determined geometry, and then, after appropriate subsequent drying and heating treatments, become rigid solids with good physico-chemical properties [11,34,35]. Therefore, it is not surprising that screw-type or hydraulic piston extruders are used to shape clays into structured materials. Moreover, although it depends on the die used, supports with many different configurations can be shaped, such as disks or pellets [36–38]. Nevertheless, honeycomb monoliths are the typical form adopted for clay-based

**Table 2**

Some examples of patents on honeycomb cordierites and related materials synthesized using clays during the last five years.

Number	Year	Title	Clay used	Clay content	Firing temp.	Running company
US 20090295007	2009	High porosity cordierite honeycomb articles from batch compositions containing non-cross-linked pore formers	N.a.	<10 wt.%	N.a.	N.a.
DE 102009001820	2009	Procedure for manufacturing cordierite ceramic honeycombs structures by extrusion, and calcining and sintering a clay mixture	Kaolin	N.a.	N.a.	Denso Corporation, Japan
DE 102009012172	2009	Procedure for producing a cordierite ceramic honeycomb structure	Kaolin	<19 wt.%	1350–1400 °C	NGK Insulators, Ltd., Japan
WO 2009070242	2009	Ceramic precursors batch composition with hydrophobically-modified cellulose ether binder for production of ceramic honeycomb at high extrusion rate	N.a.	<0.32 wt.%	N.a.	Corning Incorporated, USA
CN 101088959	2007	Method for manufacturing multifunctional honeycomb ceramic filter	Kaolin	43 mol.%	1390 °C	N.a.
CN 101074161	2007	Manufacture of aluminium-titanate-mullite multiphase honeycomb ceramic	N.a.	50–60 wt.%	1450–1600 °C	Ninguo Xianhao High-Temperature Technology Co. Ltd., PR China
WO 200711056	2007	Honeycomb structure for catalyst supports and filters and its manufacture	Layered clay	0.1–10 wt.%	N.a.	NGK Insulators, Ltd., Japan
CN 101020611	2007	Method for manufacturing honeycomb-shaped ceramic with ceramic clay and combustible granules	N.a.	40–80 vol.%	950–1800 °C	N.a.
CN 1880271	2006	Manufacture of clean light weight honeycomb ceramic furnace end with thermal shock resistance	N.a.	1–10 wt.%	N.a.	N.a.
CN 1827217	2006	Manufacture of cordierite honeycomb ceramic catalyst support for automobile exhaust gas treatment	Kaolin	43–47 wt.%	N.a.	Yixing Lvxing Catalytic Purifier Co. Ltd., PR China
CN 1730431	2006	Cordierite honeycomb ceramic for automobile exhaust gas purification	N.a.	40–48 wt.%	1350–1400 °C	Shanghai Shentai New Inorganic Material Co. Ltd., PR China
US 20060027451	2006	Fabrication of honeycomb-structured cordierite ceramics with resistance to sintering cracking	Attapulgit	N.a.	N.a.	Corning Incorporated, USA
US 20060030475	2006	Fabrication of honeycomb-structured cordierite ceramics with improved cracking resistance and reduced sintering shrinkage	Attapulgit	N.a.	N.a.	Corning Incorporated, USA
IN 1996DE02752	2005	Method for manufacturing cordierite honeycomb support by extrusion	N.a.	N.a.	1350–1420 °C	Bharat Heavy Electricals Ltd., India
US 20050221974	2005	Firing of cordierite ceramic clay for honeycomb structures without CO <sub>2</sub> production by using hydrotalcite layered double hydroxides	Kaolin and hydrotalcite	0.5–50 wt.%	N.a.	NGK Insulators, Ltd., Japan
US 20050221053	2005	Manufacture of cordierite ceramic honeycomb structures without CO <sub>2</sub> emission during firing using layered mineral precursors	Hectorite	0.5 wt.%	N.a.	NGK Insulators, Ltd., Japan
JP 2005143719	2005	Inorganic porous deodorization filter and its production method for air deodorization in gas discharge system of cooling facility	Hormite	50–90 wt.%	N.a.	Showa Mining Co. Ltd., Japan

N.a.: Not available.

extrudates due to their inherent advantages, discussed in Section 1 [31,35,39–53].

On the other hand, the preparation of structured materials by extrusion is a much more complex process than it may appear at first sight [54]. It comprises more steps than the mere shaping

mentioned above, and each step influences the quality of the final material [55]. Therefore, it is important to know the correlations between process parameters and the relevant properties of the catalysts or of the catalyst substrates that can be obtained as resulting products [4,35]. This is particularly true for extruded monolithic

ceramic catalysts if we consider that the precision required for these materials may be in the range of microns, which is much higher than that of traditional items that are also formed by extrusion of ceramic pastes, such as bricks and pipes.

According to the extensive description in literature [4,5,54,55], the fabrication of ceramic extrudates in general can be summarized in the five following consecutive steps: (i) dry mixing of the solid raw materials; (ii) wet mixing and plasticizing with water and additives; (iii) extrusion of the paste; (iv) drying uniformly; and (v) calcining at high temperatures. In the particular case of honeycomb monoliths, the structures can be prepared with many different types of cross-section and channel shape, although the most typically manufactured are circular and square. Also remarkable, in the case of clays as raw material to be extruded, it is that additives are not always necessary. Sometimes extrusion can be achieved with just water [40,42], which implies significant cost reduction, not only in terms of additives and solvents, but also the energy consumption required for further elimination by thermal treatment (step v). In this regard, it is also important to note that the preparation of non-cordierite clay-based honeycombs does not require severe final firing either. The thermal treatment determines their operational properties such as mechanical strength, specific surface area and pore structure. So, although it may change depending on the application (see below), calcination can be performed at much lower temperatures than those employed to synthesize cordierite, for example: 210 °C [40], 240 °C [44], 440 °C [41], 450 °C [53], 500 °C [46–48] or 650 °C [45].

As it is not always easy to find the adequate conditions for extrusion, especially when this is performed with a new material, preliminary studies should be developed to avoid a trial and error methodology [47]. In this sense, one of the simplest strategies reported is Casagrande's technique [9]. This enables the extrudability of the paste to be predicted by just measuring two parameters known as liquid limit and plasticity index as we have demonstrated in our lab [15,39]. This methodology is also clearly much simpler than other methods based on capillary rheometry [4] and/or structure-mechanical characteristics, which are used to investigate the formability behaviour of ceramic pastes [56]. Another refinement of the extrusion process consists of improving the final textural properties of the extrudates. In this regard, although acid activation is the conventional method employed to activate clays [57,58], in the case of clay honeycomb monoliths, attractive alternatives have recently been proposed, such as doping the clay with carbon in the first step and burning off the carbon after extrusion to create a new porosity network [41,43].

Also in the context of extrusion, it is worth noting contribution from Barannik [27]. This author has prepared composite honeycomb monoliths by co-extrusion of clays and alumina-silica finding that definite porosity control can be achieved as a function of the relative composition selected—3/2, 2/3 or 1/1. A monodisperse pore structure with extremely different pore radii or a desired bimodal pore structure can be obtained. Similar results, i.e. control of porous structures in a monolithic support without burning additives but by a variation of the ratio between the matrix materials, have been obtained by Ismagilov et al., extruding  $\text{Al}_2\text{O}_3$  with clay [22]. In both cases, the resulting materials were consequently proposed as being of interest for application in membranes.

## 2.2. Foams

Clay-based structured materials can also be prepared in the form of foams [55,59,60]. These are three-dimensional cellular structures in which the cells are connected by open windows, giving high porosity with 80–90% void space. These materials, also referred to as reticulated foams and which were originally developed three decades ago to filter out impurities from molten metals, can also

be highly suitable catalytic carriers when a low pressure drop is mandatory [59]. In fact, foams possess certain advantages with respect to the honeycombs: the possibility of a much wider range of shapes due to their preparation method (discussed below); more tortuous porosity, which improves reactant mixing and favours surface reactions; and significantly improved radial transport within the monolith. The main disadvantage is their weakness, and that is precisely the reason why, contrary to honeycombs, sintering at high temperature is systematically applied and a real ceramic obtained in all cases. Nevertheless, new processing techniques are continuously being assayed to improve their strength [55].

There are several ways to manufacture ceramic foams. Among these, the polymer sponge replication method is used mostly as it is suitable for making foams with easily accessible open cells [60]. Fig. 2 shows a simple illustration of this procedure and compares it also with that used to prepare honeycomb monoliths by extrusion. The method consists of coating an elastic open-cell polymer sponge with a slip containing the precursors of the ceramic material together with other additives. Coating is achieved by immersing the polymer sponge in to the slip, expelling the excess (e.g. by compression), and drying. Subsequently, the green body is exposed to temperature treatment. In a first stage, the organic skeleton is burned off in air. At temperatures above 1400 °C, the particles forming the ceramic replica are sintered. The cell size of the finished foam depends on the so-called pore count of the original polymer sponge and the degree of shrinkage during the drying and sintering of the green body. The phase composition of the ceramic is established by choosing the appropriate combination of raw materials and sintering temperature.

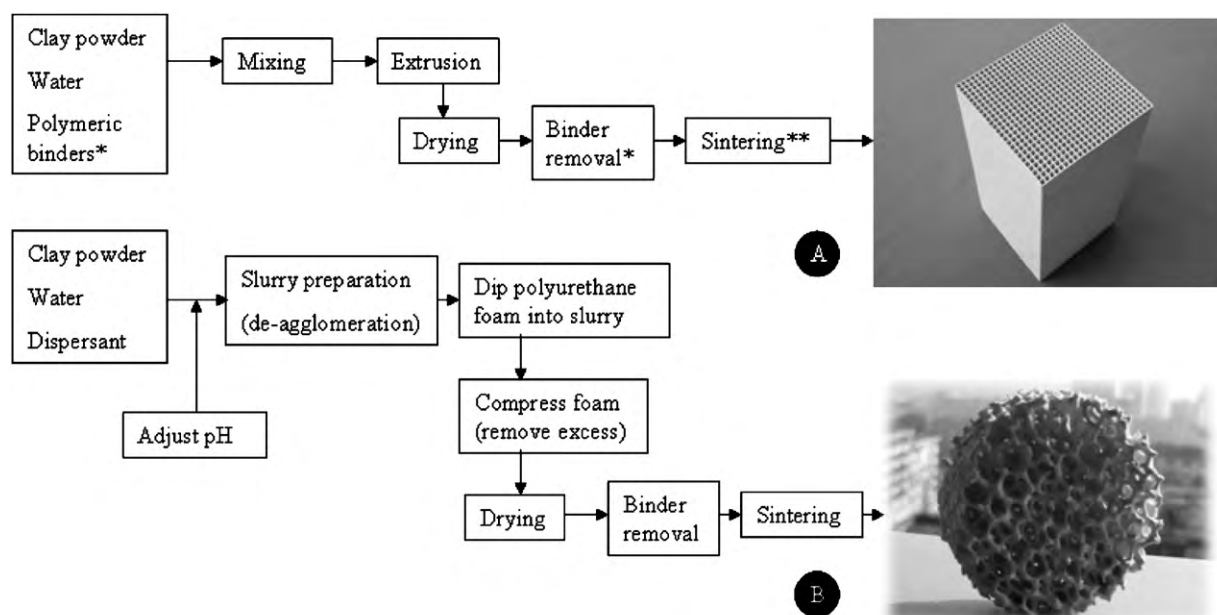
As with honeycombs, foams can also be modified, for instance coating them with oxide layers to increase their surface area or to alter the chemical nature of the surface [55].

## 2.3. Others

Besides the two major methods above described, other options can be adopted to obtain clay-based structured materials. One of them consists of depositing the clay over a preformed metallic [61] or ceramic [62,63] honeycomb to obtain what is called a clay-coated monolith, to differentiate it from the integral clay monoliths mentioned before. Coated-type monoliths are preferred when a substrate with a low surface area but high thermal stability is used so the film of clay coating permits the better further dispersion of an active phase for catalysis, while also possessing certain functionality by itself [54]. Although there are different procedures for incorporating a phase to a structured support [3,54], the most common is wet impregnation, also known as the washcoating method. This is normally selected due to its ease of use, the better control of the total amount of phase incorporated and the lower preparation time needed. This method is based on the adhesion of the phase dispersed in slurry on the monolithic surface. First, a stable aqueous suspension is prepared, by dispersing the right amount of clay-containing solid in deionised water and submitting the mixture to ultrasound for several hours. Then, a cationic polymer in aqueous solution is added to the suspension to improve its stability. The mixture is kept under vigorous stirring for about 24 h after which the monolith is immersed in it for approximately 1 min and withdrawn at a constant speed (e.g. 3 cm h<sup>-1</sup>). The excess of colloidal solution is removed by centrifugation (e.g. 400 rpm for 10 min). Then, the monolith is dried (typically at 120 °C during 1 h) and finally calcined at mild temperature (e.g. 400 °C for 2 h). To increase the amount of phase loaded on the monolith, successive coating, drying and calcination procedures can be carried out.

Finally, in the last few years, a very interesting new family of materials with a controllable structure, the so-called clay aerogels [64–66], have emerged abruptly in clay literature. They are





**Fig. 2.** Schematic diagram of the experimental procedure commonly followed to prepare (A) honeycomb monoliths, and (B) foams, from clay minerals. (\*Sometimes not necessary. \*\*Just applied for cordierite synthesis.) Photographs are taken from Jiangxi Jintai Special Material Co., Ltd.'s products catalogue.

synthesized by a method that comprises four steps: (i) a stable dispersed clay suspension is prepared; (ii) one or a mixture of amination polyhedral oligomeric silsesquioxane, alkyl ammonium salt and alkylphosphonium salt is added as an intercalation modifier; (iii) a clay gel solution with modified intercalation is obtained through ion exchange reaction, and (iv) a freeze drying technique or supercritical drying technology is used to directly carry out drying treatment on the clay gel solution to obtain the clay aerogel. This has the characteristics of large interlayer spacing (1–4 nm), a high porosity factor (50–80%), and a large specific surface area (100–800 m<sup>2</sup> g<sup>-1</sup>), and can be used as a catalyst carrier or filling, and for insulating and sound-proof materials. By adjusting parameters such as the variety and dosage of the modifier, the acidity–basicity of the gel, the synthesis process, and so on, the method can effectively adjust and control the structure, porosity factor, thermal stability and surface activity of the clay aerogel so as to meet different application requirements. Meanwhile, the preparation process is simple and does not pollute the environment, as well as being suitable for industrial production.

Table 3 summarizes the main clay mineral groups employed to prepare clay-based structured materials, depending on the design adopted. As can be deduced, although many clay minerals are present in the formulation of structured materials, montmorillonites are perhaps the most versatile type of clays. In their Ca and Na forms they are especially attractive for obtaining honeycombs by extrusion as they show no defects during drying [9,19]. In general, bentonites ensure monoliths have good radial crushing properties because their fibres are oriented in the direction of the extrusion. Moreover, associated to their layer charge, their influence on the viscosity of the ceramic paste can be finely controlled by pH [4]. Montmorillonites are also ideal for producing aerogels

due to their hydrophilic ordered nature that permits good and stable dispersion and the ability to exfoliate in the polymer used for the synthesis [65]. On the other hand, kaolinites are the most typically employed clays to create ceramic foams as they sinterize at very high temperatures so enhancing mechanical resistance, one of intrinsic weaknesses of these structures [9,55]. They are becoming more competitive in relation to other ceramic foams based on cordierite, mullite, Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub> or ZrO<sub>2</sub> [67].

### 3. Environmental applications

#### 3.1. Adsorption

Several studies have shown that non-cordierite clay-based structured materials can be good adsorbents of different pollutants, both in gas and liquid phase.

Mendioroz et al. [44] investigated mercury retrieval from flue gas by monolithic adsorbents based on sulphurized sepiolite. Sepiolite is a fibrous hydrated magnesium silicate clay that is very cheap (around €75/ton) and abundant, with unique textural and structural characteristics:  $S_{\text{BET}}$ , 150–300 m<sup>2</sup> g<sup>-1</sup>; pore volume, 0.3–0.8 cm<sup>3</sup> g<sup>-1</sup>; density, ≈0.8 g cm<sup>-3</sup>. Therefore, this material was presented as a cheaper alternative to sulphur-impregnated activated carbons, which are extremely costly sorbents in mercury control technologies. Samples of 10% S supported on monolithic sepiolite were used to retain 90 ppm mercury in air at 47 °C and ambient pressure. The honeycomb monoliths obtained were square channelled with a length of 9.5 cm and wall width of 0.04 cm as the main geometrical dimensions, and had a cell density of 34–43 cell cm<sup>-2</sup>. The experimentation was carried out in a dynamic system at flow rates in the 600–3600 cm<sup>3</sup> min<sup>-1</sup> range. A comparative study was performed of the performance of the monoliths against a fix-bed reactor of powders of 0.026 cm in size, and kinetic equations were assessed, finding the process was governed by mass transfer, under the work conditions. The importance of the adsorbents' texture and, consequently, of the preparative method for obtaining monoliths was also demonstrated. In particular, the samples' capacity per mass unit was better when impregnation was the last preparation step because porosity was better preserved and the sulphur was more uniformly distributed.

**Table 3**  
Types of clay minerals employed to prepare clay-based structured materials.

	Chlorite	Illite	Kaolinite	Montmorillonite
Monoliths	○	○	○	●
Foams			●	○
Aerogels				●

(●) Frequently; (○) occasionally.

Chafik et al. [40] tested honeycomb monoliths prepared from natural Moroccan clays on the adsorption of volatile organic compounds (VOCs). The raw material consisted of a mixture of mineral clays such as muscovite, kaolinite, vermiculite and illite, and, contrary to the authors' previous experience with other clays [39], it was easily extruded without the need for chemical binders and plasticizers. This result itself was highlighted as possibly offering a significant economic impact in terms of feedstock additives and the energy needed for their elimination. In addition, it was found of interest because it fits the recent green chemistry concept, which is required more and more nowadays in production processes involving chemistry. Moreover, the extrusion and conformation of the monoliths into rigid structures was achieved through thermal drying at moderate temperatures, yielding geometrical strength and mechanical properties that might be sufficient for VOC elimination by adsorption. The extruded monoliths presented the following geometric properties: square section of  $13.7 \text{ cells cm}^{-2}$ , wall thickness of  $0.08 \text{ cm}$  and geometric surface area of  $10.4 \text{ cm}^2 \text{ cm}^{-3}$  with an open frontal area of 49%. Besides their textural, structural and physico-chemical characterization, the adsorptive behaviour of the clay monoliths towards *o*-xylene was evaluated. The experiments were carried out at room temperature under dynamic conditions using a flow stream of  $100 \text{ cm}^3 \text{ min}^{-1}$  containing 3600 ppm of pollutant. The monoliths exhibited a total adsorption capacity around  $150 \mu\text{mol g}^{-1}$ . According to the authors, although this result could not compete with those of activated carbon [68], the most common adsorbent for VOC removal, the use of clay monoliths allowed VOC retention with, mainly, physical adsorption, which permits easier solvent recovery and adsorbent regeneration with less energy consumption. It was also concluded that monoliths extrusion with narrower channels was still needed in order to enhance the overall adsorption efficiency in terms of breakthrough time. This might help us to benefit from the important advantage of clay monoliths over activated carbon adsorbents with respect to operational safety, as they enable the suppression of the fire hazard.

More recently, the same authors [41,43] investigated the capacity of clay honeycomb monoliths, with the same configuration as above, to adsorb methylene blue from aqueous solutions. In this case, the clay employed consisted of a Spanish mixture of sepiolite, montmorillonite, kaolinite and illite-muscovite. The experiments were performed in a homemade system in which lab-scale monoliths were subjected at room temperature to a recirculated  $1200 \text{ cm}^3 \text{ min}^{-1}$  flow of the solution initially containing 10 or  $100 \text{ mg l}^{-1}$  of the pollutant. The study indicated that the adsorption capacity doubled or tripled in those honeycomb monoliths that had been prepared by mixing the clay with coal before the extrusion, and further removing the coal from the monoliths by heating them under air at a temperature as low as  $440^\circ\text{C}$ . The mechanical resistance of the monoliths in aqueous solutions remained acceptable for liquid phase applications. Consequently, the process followed in this study to activate clay monoliths was proposed as an alternative to acid activation methodologies. In particular, the results were interesting for those applications in which the combination of the honeycomb monolithic design and improvement of macroporosity may represent an advantage.

An analysis was performed of the efficiency of porous ceramic filters in the adsorption of heavy metals, lead, cadmium and chromium, present in urban residuals waters and dissolutions prepared in laboratories [60]. Filters of  $3.3 \text{ cm}$  in length,  $1.3 \text{ cm}$  wide and  $0.5 \text{ cm}$  thick were elaborated from diatomite clay (50 wt.%) mixed with other urban and industrial wastes such as bone meal and limestone. The clay came from beer industry sludge and was selected as a low cost raw material for obtaining a final adsorbent with high porosity and thermo-chemical stability while allowing the conformation into a rigid structure of a natural precursor of hydroxyapatite, a well-known immobilizer of heavy metals. For

the preparation, the authors used the polymeric sponge method to obtain porous structures, using polyurethane sponges with density of  $14$  and  $20 \text{ kg m}^{-3}$ . Milling and homogenization of the suspensions were carried out in two stages, the first one at  $500^\circ\text{C}$ , to ensure elimination of polymeric substrates and organic additives, and then at  $1200^\circ\text{C}$ , the mixture sintering point. Retention tests of heavy metals were performed in batch conditions starting from initial concentrations in a  $5\text{--}10 \text{ ppm}$  range and monitoring the evolution with exposure time. A percentage of adsorption of 98.4% was found for the lead in treated residual waters, and of 99.6% for the lead, 93.2% for the cadmium and 18.0% for the chromium in the laboratory solutions.

Also on the subject of patents, references can be found on the use of structured clays in adsorption applications. For instance, the Sharp Corporation in Japan [53] developed ceramic materials which acted as adsorbents for purification of air and water. In particular, the materials were manufactured from honeycomb-structured ceramics containing kaolinitic clays (Kibushi type), fillers such as  $\text{Al}(\text{OH})_3$  (of about  $1 \mu\text{m}$  medium particle diameter), and additives for the extrusion such as aluminium primary phosphate. The structured clayey material was fabricated by kneading the three mentioned components (the first two in a weight ratio of 1:1 to 1:9), extruding the resulting paste and then firing the honeycomb monolith in air at  $450^\circ\text{C}$  for 2 h. The final product had a large specific surface area and strength, and was also useful as a catalyst support.

### 3.2. Catalysis

In spite of the examples mentioned above, and excepting cordierite, the use as catalyst supports is still probably the most common fate of clay-based structured materials. In this regard, several different catalytic reactions in the area of environmental pollution control have been investigated.

First it is worth noting the research carried out by Bahamonde et al. [45–47] on the use of pillared clay (PILC)-based monolithic catalysts for selective catalytic reduction (SCR) of nitrogen oxides ( $\text{NO}_x$ ) by methane. This reaction was selected as noble metals on solid acids have previously shown much higher  $\text{NO}_x$  reduction rates than mixed oxides or perovskites alone. Furthermore, it is known that, like zeolites, pillared interlayer clays offer considerable Brønsted acidity, in addition to residual exchange cations which can be exchanged by metal cations from the active phases. Also, it was considered that PILCs present a tailored pore structure, perfectly tunable by exchange, which can lead to a better active phase and reactant diffusion, and finally, depending on the pillaring agent, to improvements in water vapour and  $\text{SO}_2$  resistance.

In [47] the authors introduced pillared clays, based on Spanish bentonites, as raw material to produce square-cell honeycomb monoliths with a pitch of  $3.54 \text{ mm}$ ,  $0.90 \text{ mm}$  wall thickness and a cell density of  $8.9 \text{ cell cm}^{-2}$ . A description was provided of the manufacturing conditions (paste composition) under which the resulting extruded materials offer the proper combination of physico-chemical and mechanical properties to be used as catalysts or catalytic supports. Some characterization techniques were used to control the materials' properties throughout the successive steps of preparation. Special attention was given to axial crushing strength testing in order to know the changes in the mechanical properties of the monoliths with temperature and pH. The influence of these parameters was studied bearing in mind the use of the monoliths as catalysts carriers, which require a certain contact with the solutions in which the element to be incorporated is dissolved, and also considering the subsequent thermal treatment needed to activate the supported phase. Surface areas above  $220 \text{ m}^2 \text{ g}^{-1}$  and crushing strengths above  $180 \text{ m}^2 \text{ cm}^{-2}$  were preserved in the  $2.5\text{--}9.5 \text{ pH}$  range and at temperatures up to  $500^\circ\text{C}$  when the

proper combination of ceramic paste components, 52/13/35 for Al-PILC/bentonite/water, and the applied thermal treatment were used to manufacture the monoliths.

After impregnation of the PILC monolithic supports with different noble metals, such as Rh, Pd or Pt (0.6 wt. %) [45], Bahamonde et al. performed activity tests on the SCR of NO reaction in the presence of oxygen (1.2 vol.%). The influence of the reaction temperature (300–500 °C) on methane (reducing agent) and nitric oxide molar conversions was analyzed. Other operating conditions were an initial NO concentration of 500 ppm and total flow of 3600 cm<sup>3</sup> min<sup>-1</sup>. A comparative study with zirconia-based monolithic supports was carried out, trying to correlate the catalytic activity with the physico-chemical properties of the catalysts. The results obtained indicated that structure and surface acidity of the support plays an important role in the selectivity to NO<sub>x</sub> reduction, although properties such as the surface area or pore volume could also determine the overall activity of the monolithic catalysts.

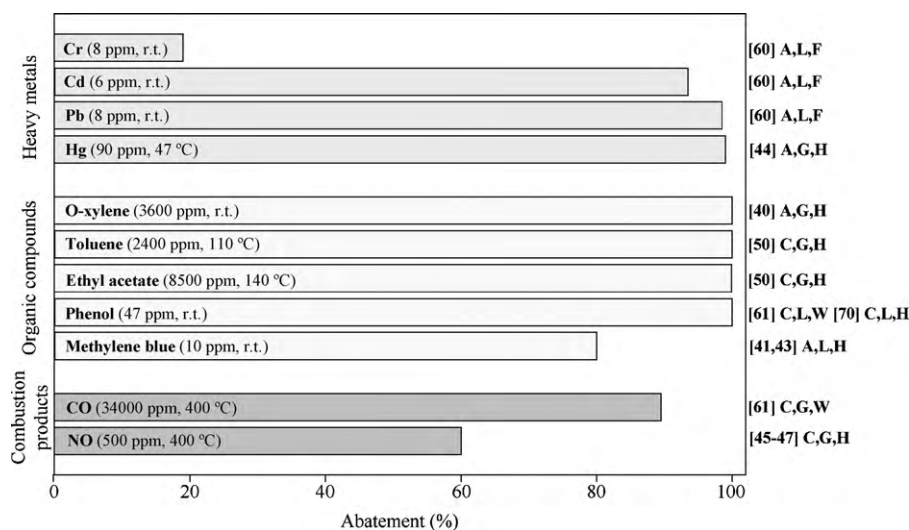
In further research [46], the same group performed a more in depth study of the catalytic system described above by using the same raw material used to synthesize the pillared clays during the preparation of the monolithic support as a permanent inorganic binder. The authors observed that this confers high surface area and acidity to the extrudates, in addition to high hydrothermal resistance and mechanical strength. The influence of the method used for active phase incorporation on the physico-chemical properties and DeNO<sub>x</sub> activity and selectivity was also studied. Conclusions were drawn from the use of different solution pH values (2.7–9.5) and precursors (acetate or chloride) of the noble metal (Pd, 0.2–0.6 wt.%) in relation to the isoelectric point of the solid.

The contribution of Rosa-Brussin et al. to the application of clay-based honeycomb monoliths for the oxidation of VOCs [48–50] is also remarkable. Starting from natural clay mixtures from Venezuela containing vermiculite, chlorite, muscovite and plagioclase, the authors extruded monoliths of 2–6 cm in length with square-shaped channels. To do this, pastes with alumina (30 wt.%) and the right amount of water to obtain plasticity of the material were first prepared. The resulting monoliths were dried at 110 °C and then calcined in air at 500 °C for 5 h. Then the monoliths were co-impregnated with aqueous solutions of salts from transition metals such as Pt, Pd, Fe and Cu. The first two were introduced to act as active phases and the two latter as promoters. In particular, three series of bi-metallic catalytic monoliths were prepared, each with two different metal compositions: Pt-Fe (0.24–4.00 and 0.13–3.50 wt.%), Pd-Fe (0.16–3.50 and 0.03–4.44 wt.%), and Pt-Cu (0.17–0.19 and 0.12–0.22 wt.%). Scanning Electron Microscopy (SEM), used to evaluate possible Pt-Fe and Pd-Fe interactions, confirmed the coexistence of these bi-metallic pairs [48]. Subsequently [49] the oxidation activity of the monoliths was tested under dynamic conditions in the presence of acetone, toluene, chlorobenzene, trichloroethylene and tetrachloroethylene. At the same time, a comparison with catalysts based on perovskite-type mixed oxides containing variable amounts of La, Sr, Mn and Co supported over the same clay monoliths was studied at the 150–300 °C temperature interval. For the noble metal-based catalysts, Pt crystals were found to be relatively large but well dispersed over the monoliths' channel walls. On the other hand, for perovskite-based catalysts, a specific activity pattern was observed for complete toluene oxidation, La<sub>0.8</sub>Sr<sub>0.2</sub>CoO<sub>3</sub> being the most active. Finally, the authors compared the catalytic activity of the structured bi-metallic catalysts Pt-Fe, Pd-Fe and Pt-Cu in the oxidation of toluene and ethyl acetate [50]. VOC concentrations were 2400 ppm for toluene and 8500 ppm for ethyl acetate. In the case of the latter, at relatively low temperatures partial oxidation products such as ethanol, ethers, acetic acid and acetaldehyde were formed, while oxidation was complete above 280 °C. For Pt-Fe catalysts, the influence of the catalytic bed size in

the activity was studied. The longest monolith (6 cm) was the most efficient, reaching toluene conversion over 90%, at an elevated flow rate (230 cm<sup>3</sup> min<sup>-1</sup>) and lower temperatures (110 °C) than those of the Pd-Fe and Pt-Cu catalysts. The existence of extensive surface zones where Pt (or Pd) and Fe were associated was determined by the SEM (mapping) technique. Iron was found to improve dispersion of Pt microcrystals, and XPS results obtained for the Pt-Fe catalyst indicated an electronic promoter effect between Pt and Fe.

Clay-coated honeycomb metallic monoliths have also proven to be useful as support for catalytic oxidation reactions. Martinez et al. [58] used a commercial type natural bentonite from Colombia as starting clay. It was first pillared with iron and then coated with gold by the deposition–precipitation method originally developed by Tsubota and co-workers [69]. After that, following the washcoating procedure described in Section 2, the above solid was deposited over a preformed stainless steel (FeCrAlloy) monolith by rolling around a spindle alternate flat and corrugated sheets, as described in [54]. The metallic monolith was a 30 mm high cylinder with a 16 mm diameter and a cell density of 55 cell cm<sup>-2</sup>. Al-Fe pillared bentonite and Au supported on Al-Fe pillared bentonite catalysts deposited on these FeCrAlloy monoliths were further characterized and tested in two oxidation reactions: gaseous oxidation of CO (in the range 25–400 °C) and phenol oxidation in an aqueous medium (at room temperature and atmospheric pressure). For the former, a mixture was used containing 3.4% CO and 21% O<sub>2</sub> in He at a total flow rate of 42 ml min<sup>-1</sup>. For the latter, a semi batch type reactor was loaded with 100 ml of phenol solution (5 × 10<sup>-4</sup> M) and a submerged monolith, bubbling air at room temperature at a constant flow (2 l h<sup>-1</sup>) with continuous stirring of the solution. A 0.1 M H<sub>2</sub>O<sub>2</sub> solution was added at a rate of 2 ml h<sup>-1</sup> during a reaction time of 4 h, with continuous adjustment of pH to 3.7 in order to improve the activity of iron species. This investigation was performed knowing previously that supporting gold on Fe and Al pillared clays results in a solid with an improved catalytic activity towards CO oxidation, due to the coexistence of active Fe and Au sites. However, no similar study had yet been performed to make the most of this advantageous monolithic design. The authors found that deposition of the solid (with and without gold) on the metallic substrate does not alter its structural characteristics. Also, the use of monoliths improved the activity in the reactions, both in the gas phase (CO) and the liquid phase (phenol), with this improvement being more evident in the oxidation of phenol. In addition, the use of a structured support in the reaction taking place in aqueous medium offered the additional advantage of facilitating the separation of the catalyst from the reaction medium.

Another interesting reference is the very recent paper by Sanabria et al. [70]. Extrudates developed from AlFe and AlCeFe pillared bentonites were shaped as pellets, Raschig rings and cylindrical honeycomb monoliths and tested as catalysts in the oxidation of phenol. Na- or Ca-bentonite was also used as binder. The extruded pellets had a diameter of 1.96 mm and were cut to lengths of around 6 mm. The Raschig rings, with an internal diameter of 4.25 mm and an internal diameter of 1.96 mm, were also cut to a length of 6 mm. The cylindrical monoliths had an outside diameter of 16.25 mm, a wall thickness of 0.85 mm and square open channels of 1.72 mm. This gave a cell density of 11.7 cells cm<sup>-2</sup>. These monoliths were cut to lengths of 15 mm. The mechanical stability of the extrudates, measured as breaking force, was evaluated as a function of thermal treatment (105, 400 and 500 °C) together with the stability to water immersion. Calcination at 500 °C was needed to obtain water stable materials. The specific surface area and the micro- and mesopore volume of the extrudates depended on the calcination temperature as well. Regarding catalytic activity, the tests were performed at 25 °C and atmospheric pressure in the following way: (i) in the case of pellets and Raschig rings, a glass thermostated semibatch reactor, with 4 plastic mesh bas-



**Fig. 3.** Maximum degree of pollutant abatement (%) reported in references discussed in this review (number in square brackets) as achieved by using non-cordierite clay-based structured materials. Values in brackets indicate the initial pollutant concentration and reaction temperature. Letters after bibliographic reference denote other experimental conditions: A, adsorption; C, catalysis; F, foams; G, gas phase; H, honeycomb monoliths; L, liquid phase; W, washcoated monoliths.

kets attached to a stainless steel shaft connected to a motor, was used; (ii) in the case of monoliths, these were packed between two layers of glass Raschig rings inside a fixed bed reactor with a phenol recirculation flow of  $150 \text{ ml min}^{-1}$ . For the reaction, 250 ml of a  $5 \times 10^{-4} \text{ M}$  phenol solution, 2.08 g of extruded material and a solution of  $0.1 \text{ M H}_2\text{O}_2$  ( $20 \text{ ml, } 2.22 \text{ ml h}^{-1}$ ) was used, adjusting the pH of the reacting medium to 3.7. The conversion rate for phenol oxidation of the extrudates was generally lower than for powders, due to an increased induction period and diffusion limitations. It was also lower than that reported in [61] for similar experimental conditions, but it should be noted that clay, and no supported metal, was the active phase in this study.

As with adsorption applications, the use of non-cordierite clay-based structured materials in catalysis is also present in patented works. As an example, Yao and Kimble from the Conocophillips company in USA [71] demonstrated that carbon monoxide can be selectively oxidized to carbon dioxide in a feedstream containing hydrogen over a catalyst based on platinum and iron (molar ratio from 0.5:1 to 4:1) supported on clay monoliths at  $60\text{--}100^\circ\text{C}$ . The deactivated Pt-Fe catalyst was regenerated by increasing the temperature to  $175\text{--}225^\circ\text{C}$ . The paper concluded that these catalysts were useful at removing CO for manufacturing  $\text{H}_2$ -rich fuel gas streams for fuel cells.

Fig. 3 summarizes the main results obtained using non-cordierite clay-based structured materials in environmental applications that have been discussed in this review. This figure illustrates the wide range of applications and the efficiency of clays in these structured systems.

#### 4. Conclusions

Nowadays there is a great deal of evidence that clay-based structured materials are very attractive. They can be prepared with good control of final properties in many different ways, such as in the form of honeycomb monoliths (either integral or coated), foams or aerogels. Actually, the capacity to design tailor-made structured clays has improved so much in recent decades that they have become very versatile materials, even being competitive in some cases with activated carbons and zeolites. This is particularly true for environmental applications and, as an example, they are very efficient at removing heavy metals, CO,  $\text{NO}_x$  and VOCs. For these uses they may act as adsorbents but also as suitable catalytic sup-

ports and even active phases for catalysis in some cases, both in liquid and gas phase, and operating in a wide range of pollutant concentrations.

Nevertheless, the technological use of clays at an industrial scale is still very restricted to cordierites. Most of the knowledge around is patented and the property of multinational companies, and the information published on other structured clayey materials is much more scarce in comparison.

The fact that clays are so cheap and abundant, their easy handling, low toxicity and high stability in oxidant ambient at high temperature, and the ever-growing list of possibilities to easily enhance their inherent properties, should be convincing enough reasons for humanity to keep searching new ways to exploit this familiar resource. In this sense, the use of non-cordierite clay-based structured materials for the benefit of the environment is the best example in a world which is always more in need of urgent low cost solutions. Moreover, beyond the applications mentioned above, the development of clay aerogels is particularly attractive, as pointed out by Schiraldi's group. The tremendous potential of these ultra-low density, strong and flexible materials not only adds value to clays enabling the manufacture of high tech "green" kitty litters, but much more. They could for example be used as adsorbents for cleaning up oil spills or as catalyst supports, an application that certainly deserves more study. Definitively, like Schiraldi, we have also seen the future and it is clay.

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