Preparation and Characterization of New Products Obtained by Pillaring Process

NICOLETA PLATON1*, ILIE SIMINICEANU2, NECULAI DORU MIRON1, GABRIELA MUNTIANU1, RAMONA MIHAELA ZAWADA1, GABRIELA ISOPENCU1, IILEANA DENISA NISTOR1

1 University "Vasile Alecsandri" of Bacau, Engineering Faculty, 157 Calea Mărășești, 600115, Bacau, România
2 Technical University "Gh. Asachi" of Iași, Faculty of Chemical Engineering and Environmental Protection, Department of Chemical Engineering, 73 Mangeron Blvd., 700050, Iasi, Romania
3 Politehnic University of Bucharest, Faculty of Applied Chemistry and Materials Science, 313 Splaiul Independenței, 060042, Bucharest, Romania

This paper proposes a simplified method of pillaring of clays with iron to obtain new products, efficient catalysts in phenol degradation processes. The process uses a minimum duration and is much easier to operate than the conventional method of pillaring. The intercalated clay was aged using microwaves. To simplify the preparation of pillared inter-layered clays (PILC), we used clay, without purification or chemical pre-treatment in the laboratory. We described the optimum obtaining conditions of Fe-pillared clays using a method that demand lower duration and expenditure, offering the potential for extension to an industrial scale. The starting materials used to prepare the pillared clays were: sodium bentonite, montmorillonite KSF and montmorillonite K10 provided by Sigma Aldrich. The starting clays and pillared clays were characterized by N. adsorption-desorption isotherms, measurement of the specific surface area, infrared spectra (FTIR) and SEM-EDAX analysis.

Keywords: Fe-pillared clays; industrial pillaring process; Na - bentonite, microwave aging.

Barrer and MacLeod first introduced the concept of lamellar solid transforming into porous structures by inserting laterally spaced molecular props between the layers of a smectite clay mineral. The terms "pillared" and "pillaring" are originally from the work of Brindley& Semples and Vaughan & Lussier published in the 1970 [1] on smectite-type clay minerals. They found that thermally stable, robust inorganic moieties could be intercalated between the individual clay platelets of the stack or aggregate of clay lamellae. The mechanism was proposed to be an ion exchanged reaction, followed by solvent removal [2]. During calcination, the metallic polyhydroxocation is transformed into an oxide which fixes itself to the clay into a strong manner. The introduction of pillars, besides increasing the material resistance and stability, provides porosity, a greater surface area access to acid areas existing in natural clay, and the presence of potentially active species for a specific reaction [3].

Through pillaring process, clay layered compounds are transformed into thermally stable micro-and/or mesoporous materials with retention of the layer structure. The material obtained is a "pillared compound" or a "pillared layered solid". Pillared inter-layered clays (PILC) have attracted increasing attention, particularly from industry since 1970s, because of their microporous nature and catalytic potential. The pillaring methods developed until now, in the laboratory, are difficult to extend to industrial scale, because they are expensive, laborious and time-consuming [4-9]. However, PILC with iron have not been used as catalysts at industrial level.

The Fe - pillared clay minerals were proposed in 1988 by [10] as an analogy to Al - pillared minerals. However, the interactions between Fe (III)- hydrated ions and the parent mineral clay are not well known. Some authors found the basal spacing of Fe – pillared minerals clay to be > 2 nm in calcined form, i.e. 0.5 nm higher than that of parent mineral clay. This indicates the incorporation of a polycation with a height of about 1 nm, but such cations have not been isolated [11-15]. Some skepticism as to the ability of Fe ions to produce ordered pillared clay structures was explicitly stated by some authors [6, 16].

The conventional laboratory method of Fe-PILC synthesis is essentially based on mixing a diluted clay suspension with a diluted pillaring solution [4,17,18]. This laborious, expensive, and time-consuming procedure involves the following steps: clay purification clay drying; slow addition of the pillaring solution (24 hour - one month); ageing diluted pillaring solution; washing with deionised water until chloride free and filtration; final heating of the dried clay (calcination) [4,7,13].

To produce pillared clays at an industrial scale, the above procedure must be simplified. For simplifying the Fe-PILC preparation in the laboratory we use unpurified clay and microwaves ageing. The use of microwave irradiation during intercalation offers, against conventional preparation, the advantage of the time decreasing of PILC preparation. We described the optimum obtaining conditions of Fe-pillared clays using a method that demands lower duration and expenditure, offering the potential for extension to an industrial scale.

Experimental part

Materials and methods

Mineral clays used as starting materials are: Na-bentonite B 3378, montmorillonite KSF and montmorillonite K10 provided by Sigma Aldrich. To obtain the pillaring solution we used NaOH and FeCl3 . 6H2O (Lach-ner) and for ion exchange reaction NaCl.
Methods

The simplified pillaring method proposed in this paper was carried out following the stages: homoionization of clay with a sodium chloride solution, intercalation of the pillaring agent (previously obtained) in a aqueous clay suspension 2 % (% mass.), ageing, washing, drying and calcination of the intercalated clay. For Na–bentonite case, the stage of homoionization with sodium chloride solutions was removed, because this is natural sodium clay. Two pillaring methods, a conventional – A - uses room temperature (fig. 1) and a simplified method which use microwaves ageing – B (fig. 1) were carried out and compared.

Ion exchange

KSF and K10 montmorillonites clays were homoionized with a NaCl solution 2M, with a solid: liquid ratio of 1:50 (10 g clay/500 mL NaCl). The ion exchange was realized at 353 K and was repeated three times. After each process, the clay was washed with distilled water until no chloride ions were found. To avoid the rapid evaporation of the water, the ion exchanged samples were slowly dried at 333 K for 24 h.

Preparation of the intercalation pillaring agent

The polyhydroxocationic solution that contains Fe, was prepared using a molar ratio (OH/Fe) of 2.2. This was prepared by drop-wise addition of a NaOH solution to a FeCl₃ ∙ 6H₂O solution, at room temperature with vigorous stirring. The stirring during the addition of NaOH was necessary to prevent local accumulation of hydroxyl ions, which invariably produce precipitation of iron hydroxy[7, 9, 19]. The intercalation solution precipitated using NaOH 0.4 M and FeCl₃ 0.2 M. This impendim was removed by using dilute solutions of NaOH (0.2 M) and of FeCl₃ (0.2 M). A temperature of 333 K during the preparation of the pillaring agent determines precipitation, unfavorably for the obtaining process of the pillaring solution. Instead, using lower temperatures this disadvantage was removed and the cost of pillaring process is diminished at energetic consuming level.

The pillaring agent prepared in laboratory was aged by two methods: the classical method of aging (at room temperature) and with microwaves. Towards the influence of the duration of aging on the PILC synthesis, in this paper was presented an ageing method for the solutions intercalation that decreases the aging duration from several weeks (by the classic method) to several minutes (5-10 minutes); the last method used microwave irradiation (160 W).

Intercalation

The intercalation was carried out at 333 K by slow addition of the pillaring agent (obtained previously) over a suspension of 2 % clay (% mass.); the stirring duration was one hour. A pillaring stoichiometry of 4 mmol Fe/g clay was used. The intercalation process was carried out under constant stirring and, after the consuming of the pillaring agent, the clay dispersion was stirred during 3 h at the same temperature.

The classical method of the intercalated clay aging was carried out at room temperature from one to seven days in the presence of the mother liquor. The microwave irradiation ageing method was carried out for 5, 10 and 15 minutes (at 160W power level). After ageing, intercalation of the pillars is improved by repeated washing with water until free of chloride ions. The solid was recovered by filtration, dried at 393 K in steps: keeping one hour at 313 K, one hour at 333 K, one hour at 353 K, etc., finishing at 393 K.

Calcination

The calcination was carried out after drying at 673 K for 2 h. The solids obtained after calcination were grounded and labelled.

Methods of characterization

The textural characteristics of clays before and after pillaring were determined from N₂ adsorption/desorption
isotherms at 77 K using Quantachrome Autosorb - 1-MP Surface Area and Porosity Analyzer.

The FTIR spectroscopy analyses were done using a FTIR Bruker Tensor 27 apparatus.

The SEM – EDAX analysis were realized with a SEM apparatus with integrated EDAX of type Philips XL 30.

**Results and discussions**

The starting clays and pillared clays were characterized texturally (analysis of the N₂ adsorption-desorption isotherms and of the specific surface areas by BET method); structurally (analysis of the FTIR spectra) and by chemical composition (the analysis SEM-EDAX).

**Analysis of nitrogen adsorption/desorption isotherms and of specific surface area**

These analyses were done in order to determine the influence of chemical modification of clays (natural sodium bentonite, montmorillonite KSF and montmorillonite K10) on the structural characteristics of those. Before analyses the samples were automatically degassed under vacuum for 4 h at 475 K; the sample mass varied between 0.3418 g ad 0.2453 g.

The adsorption-desorption isotherms are important due to the parameters that can be established: specific surface area, porosity, pore volume, pore size distribution (PSD) and average pore diameter (APD). More, we can obtain also qualitative information regarding the structure (pores shape, interconexions etc.). To determine the textural characteristics are proposed several models that will be discussed after. The adsorption-desorption isotherms with N₂ of Be-Na and of a typical catalyst for this paper, respectively M₀₋₁₀ Be-Na-Fe, are shown in figures 2 and 3. The comparison between the experimental isotherm (fig. 1) and the typical IUPAC forms published in reference books [20-22], lead to a type IV isotherm with H1 hysteresis. This means that the analysed material is mostly mesoporous. The hysteresis H1 has a narrow loop with two branches almost vertical and parallel. This form of hysteresis is often associated with adsorbents made up of agglomerates leading to narrow pore size distribution (PSD).

Table 1 summarizes the results of the specific surface areas (determined by BET method) for the different ageing durations

The surface area of the catalyst is the main factor that influences the catalytic activity [5, 18, 23]. The major transformations induced by Fe-pillaring were: the surface area increases from 37.5 m²/g for Be-Na to 139.6 m²/g for M₀₋₁₀ Be-Na-Fe, while the average pore size decreased from 15.4 nm in Be-Na to 5.85 nm in M₀₋₁₀ Be-Na-Fe. Both materials were mostly mesoporous.

Table 1 summarizes the surface areas of PILC obtained from Be-Na in the case of using in ageing processes microwave irradiation; we observe the effectiveness of this technique. PILCs obtained from montmorillonite KSF and K10, show a decrease of the surface area related to

<table>
<thead>
<tr>
<th>Starting clays</th>
<th>Pillared clays</th>
<th>Conditions of ageing</th>
<th>Specific surface area, m²/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na-bentonite</td>
<td>A₁₅₁Be-Na-Fe</td>
<td>A₁ - one day at room temperature</td>
<td></td>
</tr>
<tr>
<td></td>
<td>A₁₅₁Be-Na-Fe</td>
<td>A₇ - 7 days at room temperature</td>
<td></td>
</tr>
<tr>
<td>M₀₋₁₀Be-Na-Fe</td>
<td>M₀₋₁₀ min. at microwave I.A.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>M₀₋₁₀Be-Na-Fe</td>
<td>M₁₀₋₁₀ min. at microwave I.C.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>M₀₋₁₀Be-Na-Fe</td>
<td>M₃ - 5 min. at microwave I.A.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>M₀₋₁₀Be-Na-Fe</td>
<td>M₁₀₋₁₀ min. at microwave I.C.</td>
<td></td>
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</tr>
<tr>
<td>M₀₋₁₀Be-Na-Fe</td>
<td>M₁₀₋₁₀ min. at microwave I.A.</td>
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<tr>
<td>M₀₋₁₀Be-Na-Fe</td>
<td>M₁₀₋₁₀ min. at microwave I.C.</td>
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</table>

**Table 1**

SPECIFIC SURFACE AREAS FOR DIFFERENT TIMES OF AGEING
the surface area of the starting material. This shows that beyond the ageing method, the nature of the raw material has also an important role. However K10 and KSF show higher surface areas than Be-Na 106 m²/g and 240 m²/g in comparison with 37.5 m²/g, but the PILCs obtained (after pillaring with Fe³⁺) have a lower specific surface area than that of raw materials. Therefore, using as raw material clays previously activated (K10 and KSF), which presents higher surface area than the untreated clays (Be-Na), we can obtain, by Fe³⁺ pillaring, materials with lower specific surface area.

Table 2 plotted the duration of each stage of the obtaining process iron pillared clays by conventional method (A) and by microwaves ageing (B), the degree of time abatement and specific surface area.

FTIR spectroscopy

The results show after clay pillaring a small decrease in the peak intensities of the band at 470 cm⁻¹ corresponding to Al-O stretching and a shift of Si-O-Si stretches vibration at 1033 cm⁻¹ towards slightly higher frequency. The intensities bands at 917 cm⁻¹ (OH-deformation linked to Al³⁺) and 848 cm⁻¹ (OH-deformation linked to Al³⁺, Mg²⁺) decreased with pillaring [12]. This observation is related only to the PILC obtained from Be-Na respectively M₀.10 Be-Na-Fe (fig. 4).

**Table 2**

<table>
<thead>
<tr>
<th>Stage</th>
<th>Duration of A1A1Be-Na-Fe obtaining by Procedure A</th>
<th>Total duration - Procedure A</th>
<th>Duration of M₀.10Be-Na-Fe obtaining by Procedure B</th>
<th>Total duration - Procedure B</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Ion exchange</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 2 plotted the main advantages of method B in rapport with method A: beside the lower duration, the materials produced by method B have a higher specific surface area than the material prepared by method A.
After pillaring result a small band at 3000 cm⁻¹ due to OH-stretching of bonded metal ions. The peak at 3640 cm⁻¹, which was ascribed to the metal-OH stretching in the octahedral layer, decreased with pillaring, while the broad band at 3440 cm⁻¹ corresponding to interlayer/adsorbed water on the surface became dominant. The interlayer water band at 3224 cm⁻¹ completely disappeared after pillaring [12]. Comparatively with M₆₀⁻¹₀Be-Na-Fe (fig. 4), the samples derived from KSF (fig. 5) and K10 (fig. 6) do not present these characteristics, showing that the pillaring process was realized only in the first case. Figure 3 shows that band from 3620 cm⁻¹ (fig. 4), (typical of smectites with large amount of Al in the octahedral layer) decrease after pillaring [12]. Formation of a new band in the range of 3740-3770 cm⁻¹ (fig. 4) is an important observation. The identification of hydroxyl species on pillared clays is extremely difficult, because of the complexity of the system and the opaqueness of the sample

<table>
<thead>
<tr>
<th>Preparation of the intercalation pillaring agent:</th>
<th>4 h 28’</th>
<th>4 h 28’</th>
<th>4 h 28’</th>
</tr>
</thead>
<tbody>
<tr>
<td>- drop-wise addition of a NaOH solution to a FeCl₃·6H₂O solution (1.5-2 mL/min.)</td>
<td>28 h 28’</td>
<td>28 h 28’</td>
<td>28 h 28’</td>
</tr>
<tr>
<td>- aging of pillaring solution (room temperature)</td>
<td>24 h</td>
<td>0’ (microwaves)</td>
<td>0’ (microwaves)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Intercalation</th>
<th>4 h 44’</th>
<th>4 h 44’</th>
<th>8 h 54’</th>
</tr>
</thead>
<tbody>
<tr>
<td>- preparation of a 2% clay suspension by stirring</td>
<td>1 h</td>
<td>1 h</td>
<td>1 h</td>
</tr>
<tr>
<td>- slow addition of the pillaring solution over the clay suspension (2-3 mL/min.)</td>
<td>32 h 44’</td>
<td>32 h 44’</td>
<td>32 h 44’</td>
</tr>
<tr>
<td>- stirring of the dispersion of clay and pillaring agent at 60°C</td>
<td>3 h</td>
<td>3 h</td>
<td>3 h</td>
</tr>
<tr>
<td>- aging of the clay dispersion with the pillaring agent (room temperature)</td>
<td>24 h</td>
<td>10’ (microwaves)</td>
<td>10’ (microwaves)</td>
</tr>
</tbody>
</table>

| Filtration and washing with distilled water | 3 h | 3 h | 3 h |

<table>
<thead>
<tr>
<th>Steps drying:</th>
<th>7 h</th>
<th>7 h</th>
<th>7 h</th>
</tr>
</thead>
<tbody>
<tr>
<td>- 1 h at 40 ºC, 1 h at 60 ºC, ......120 ºC (heating rate: 1 degree/min.)</td>
<td>7 h</td>
<td>7 h</td>
<td>7 h</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Calcination</th>
<th>2 h 50’</th>
<th>2 h 50’</th>
<th>2 h 50’</th>
</tr>
</thead>
<tbody>
<tr>
<td>- at 400ºC (heating rate: 8 degree/min.)</td>
<td>2 h 50’</td>
<td>2 h 50’</td>
<td>2 h 50’</td>
</tr>
</tbody>
</table>

| Total duration (hours) | 74.02 | 26.12 |
| Degree of time abatement (%) | - | 64.71 |
| Specific surface area (BET method) | 120.3 | 139.6 |
in the corresponding IR region. It has been reported that isotopic exchange with mild deutering agent C$_6$D$_6$ has allowed identifying two acidic hydroxyls, with OH stretching modes at 3660 cm$^{-1}$ - 3740 cm$^{-1}$. The first structure formed is referring to the unstructured band of the parent montmorillonite and the next its determined by the sealing of montmorillonite layer during pillaring process [24].

For Be-Na we observe an elimination of the impurities from M$_{0-10}$Be-Na-Fe by Si-O stretching vibration of a cristobalites 1092 cm$^{-1}$, 796 cm$^{-1}$. This idea was confirmed by the literature [25].

In conclusion, microwave irradiation during intercalation offers, against conventional preparation, the advantage that the impurities present in the original clay are eliminated.

**SEM-EDAX analysis**

EDAX analysis was realized concomitant with SEM in two points for the raw material (Be-Na) and for a representative material (M$_{0-10}$Be-Na-Fe) from structural and catalytic point of view.

The results obtained are showed in tables 3, 4 and figure 7. The SEM-EDAX analyses were realized in two distinct points.

In this work, the EDAX-SEM analysis shows a uniform distribution of the iron in pillared clays. The two analyzed points (tables 3 and 4) show an equivalent content of Fe, this indicates that the preparation method is efficient for obtaining active metal species very well dispersed in the clay matrix. The content of Si has an average of 17.54 %, Si is a component specific for clay that forms the clay layers; the Si amount is modified indicating only the fact that the relative proportion related to other components is modified because of the introduction of a new component (iron).

**Conclusions**

The Fe$^{3+}$ pillaring simplified method proposed in this work (fig. 1 B) is much advantageous than the classical pillaring process (fig. 1 A) due to:

- the elimination of ion exchange stage of the starting clay, Na - bentonite chemically unmodified;
- the elimination of the stage of ageing of intercalation;
- the ageing duration intercalated clay is only of 10 minutes by utilization of microwave irradiation.

The use of Na - bentonite is indicated in obtaining pillaring clays because, by elimination of the ion exchange stage and of some laborious time and energy-consuming stages, contribute to the deceasing of the PILC price.

The use of microwave irradiation during intercalation offers, against conventional preparation, the advantage of time decreasing of PILC preparation.
The method A of room temperature pillaring solution ageing generate materials with specific surface area lower than the materials obtained using method B. Also, we propose method B with microwave ageing for obtaining, in a short period of time, iron pillaring clays with better textural properties (degree of time abatement of 64.71% in rapport with method A).

Using the simplified method previously described new advanced catalysts are obtained for phenol oxidation in diluted aqueous medium.

References
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