INFLUENCE OF CERIUM ADDITION ON THE SYNTHESIS OF SOLIDS BASED ON PLATINUM SUPPORTED OVER ALUMINA-PILLARED CLAY

Influencia de la adición de cerio en la síntesis de sólidos a base de platino soportado sobre arcilla pilarizada

ABSTRACT

The present work shows the preparation and characterization of a set of solids by modification of a natural clay with Al, Ce and Pt. The characterization of the solids by X-ray diffraction (XRD) reveals the insertion of alumina pillars, whereas the subsequent impregnations of the pillared clay with Pt (II) or Ce (IV) do not lead to structural variations that can be observed by XRD. The characterization by nitrogen adsorption indicates that the incorporation of platinum species originates damages in the microporosity of the solid, while the addition of cerium prevents the deterioration of the textural properties.

KEYWORDS*:* Pt-Ce catalyst, Al-pillared clays, Pt-impregnation, microporous materials.

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RESUMEN

El presente trabajo muestra la preparación y caracterización de un conjunto de sólidos mediante la modificación de una arcilla natural con Al, Ce y Pt. La caracterización de los sólidos mediante difracción de rayos X (DRX) revela la inserción de pilares de alúmina, mientras que la posterior impregnación de la arcilla pilarizada con Pt(II) o Ce(IV) no conduce a variaciones estructurales observables por DRX. La caracterización mediante sortometría de nitrógeno indica además que, la inserción de especies de platino ocasiona un detrimento en la microporosidad del sólido, mientras que la incorporación de cerio previene el deterioro de las propiedades texturales.

PALABRAS CLAVE: *Catalizadores de Pt-Ce, arcillas pilarizadas con Al, impregnación con Pt, materiales microporosos.*

1. INTRODUCTION

The development of intercalation processes in clay minerals, with inorganic structures, and the first synthesis strategies on pillared clays like interesting microporous materials (molecular sieves), around the middle of 1970, generated new research alternatives (in Inorganic Chemistry and Solid State Chemistry) towards the materials preparation with adsorbent or catalytic properties, as well as with molecular separation properties [1-6]. The application field of these materials is wide, due to the possibility of intercalating different types of pillars, making them suitable to specific processes of adsorption or catalysis. The introduction of inorganic pillars, in addition to improving the resistance and stability of the clay mineral, increases the microporosity and provides a higher surface area in the solid, allowing the accessibility of reagents towards potentially active sites in the catalysis of some reactions.

The general procedures of synthesis of pillared clays have been widely studies and reported in literature during the last years [1,3, 6]. In general, the synthesis require starting materials with good expansion capacity to let the access and exchange of large inorganic species into the mineral interlayer spacing, which is a recognized property of smectitic materials. Pillaring of clay minerals with aluminum polyhydroxocationic species having keggin structure, $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$, has been the most investigated, revealing a series of parameters to be strictly controlled in this process [4, 6, 7]; for example: the metal concentration and the OH/metal ratio in the intercalating solution, the concentration of clay suspension, pH, temperature and aging time of the intercalating solution or the intercalated material.

The operation of this type of solids in the different applications (adsorption, separation or catalysis) requires of satisfactory structural and textural properties, for which the control of the microporosity (size, volume and shape of pores) and the surface area are crucial aspects, since such parameters determine and limit the successful use of these materials [5]. In heterogeneous catalysis, the shape and size of pores may control the diffusion of the

reagents towards (and from) the active sites in the solid, determining the activity and selectivity of the catalyst.

On the other hand, platinum-supported catalysts have been widely studies and used in several applications, in which the most employed support is the alumina [5]. Recently, some papers reported the impregnation of Pt on pillared clays to be employed as catalysts in the CO combustion and the complete oxidation of acetone and methyl ethyl ketone [5, 8-9], volatile organic compounds (pollutants) frequently found in several chemical industries.

The present work shows the preparation and characterization of a set of solids synthesized by modification of a natural clay (saponite, from Yunclillos-Spain) with aluminum, cerium and platinum, to obtain active catalysts that would be used, later on, in the catalytic combustion of carbon monoxide and volatile organic compounds (VOC), two environmental interesting reactions [8-11]. However, the main contribution of this paper is to assess the effect of impregnation of Pt, with and without the previous incorporation of cerium, on the structure and texture of aluminum-pillared saponite, to find alternative synthetic routes that allow to prevent the deterioration of the structural and textural properties of the final catalysts due to the impregnation of the noble metal.

2. EXPERIMENTAL

2.1. Synthesis of pillared clay:
The starting material is a natural clay from Yunclillos (Spain), whose main component has been identified as a saponite, with the following chemical composition: SO_2 55.29%, Al_2O_3 5.40%, Fe_2O_3 1.43%, MgO 25.23%, TiO_2 0.15%, CaO 0.41%, Na_2O 0.75%, K_2O 0.30% and MnO 0.026% [12].

The pillaring solution (a solution of the keggin polyoxocation $[Al_{13}]^{7+}$) was prepared by slow addition, at room temperature, of a 0.2 M solution of NaOH (Merck 99.0 %) to a 0.1 M solution of Al^{3+} ($Al(NO_3)_3$.$9H_2O$ Merck 95.0%) in vigorous stirring, using a 2.4 OH^-/Al^{3+} molar ratio and reaching a pH of 4.0 at the end of NaOH addition. The final solution was aged for 48 hours at 40°C [5].

The pillaring process was developed by ionic exchange of the saponite clay with the keggin-polyoxocation solution at 40°C, adding the pillaring solution (dropwise) to a clay suspension (2%); the clay was previously swelling for 24 hours. After addition, the mixture was left in continuous stirring for 2 hours at the same

temperature; then, it was cooled at room temperature to continue stirring for 48 hours. Finally the suspended solid was washed by dialysis (membrane Spectrapor) until nitrate free. The final material was dried at 80 °C for 4 hours and calcined at 400°C for 2 hours using an adequate heating ramp [5].

2.2. Cerium incorporation in the pillared clay:
A wet impregnation (the sample was previously outgassed and then placed for 5 hours in rotavapor) with a $(NH_4)_2[Ce(NO_3)_6]$ solution (initial reagent Merck 99.0 %) was realized in order to incorporate cerium (probably as cerium oxide). An appropriate volume of solution to obtain a quantity of cerium around 2% was added to the pillared clay. Finally the solids were dried at 80°C.

2.3. Pt impregnation on the pillared clay and on the pillared clay modified with cerium:
The platinum impregnation was carried out in a rotavapor, placing a previously outgassed sample (2 hours at 80°C in vacuum) and adding the required quantity (incipient impregnation) of platinum (II) acetilacetonate (Aldrich, 97%) solution in dioxane (Merck, 99.5%). The mixture was left in contact for 24 hours at room temperature. The solid was dried at 80°C for 2 hours and then calcined at 500°C for 2 hours. The resulting solids are designated as Al-PilC to the pillared clay and indicating the platinum quantity (%) incorporated in each case.

2.4. Solids characterization
X-ray diffraction analyses (XRD) were realized using a PW 1820 diffractometer, with 2θ geometry and Kα radiation of Cu (λ=1.54056Å), by forced powder technique, a step size of 0.05 and a step time of 2 second.

The textural properties of the solids were determined by nitrogen adsorption analysis at 77K on the samples previously outgassed at 300 °C and pressure below 5 x10^{-2} mm-Hg for 12 hours, using an automatic instrument Quantachrome autosorb 1. The adsorption isotherms were obtained in the P/P_0 range between 10^{-5} and 0.99. To determinate the BET surface areas the approach proposed by Remy and coworkers [13] was employed. The micropore volumes were determined by t-plots (with Halsey's equation to calculate the t-values) [14-16]. The total volumes of pore were measured by the Gurvitsch method at P/P_0=0.99 [15].

The platinum content in the solids was determined by atomic absorption spectroscopy in a Varian A10 spectrophotometer.

3. RESULTS AND DISCUSSION

X-ray diffraction results show the increase in the basal spacing (d_{001}) value in the pillared solids with respect to the natural saponite not calcined, which indicates the effective modification of the natural clay by the introduction of alumina pillars (figure 1 and table 1). Chemical analysis indicates the incorporation of Pt (0.40%, 1.08%, 0.52% y 1,09%) in the solids as it is showed in table 1. As in the solids modified with Pt as in those modified with Pt-Ce no characteristic XRD signal of chemical species from this metal was observed, probably due to the incorporation of relatively too small quantities to be detected by X-ray diffraction in a clay matrix. Besides, the XRD analysis reveals the conservation of the alumina-pillared clay structure after the impregnations with Pt or Pt-Ce and subsequent calcination (figure 1).

The textural analysis shows the formation of microporosity as consequence of the pillaring of the natural clay. Figure 2a reveals the increase of the adsorption capacity of the pillared saponite regarding the natural material. However, the incorporation of Pt leads to the decrease of such adsorption capacity, whereas the cerium incorporation (most likely as CeO_2) maintains stable this property in the solids (figure 2b).

The effect of Pt and Ce on the texture of the pillared clay is confirmed by means of the determination of BET surface areas applying the approach proposed by Remy and coworkers [13], the determination of micropore areas and volumes by t-plots (Lippens and De Boer) [14] and the measure of total pore volumes by Gurvitsch [15]. Table 1 and figures 3a and 3b reveal an important detrimental effect on the textural properties of solids as consequence of platinum impregnation. It is observed, in all cases, that the micropore volumes and surface areas (micropore areas, external areas and total areas) clearly decrease as consequence of the Pt impregnation. Nevertheless, the previous incorporation of cerium in the
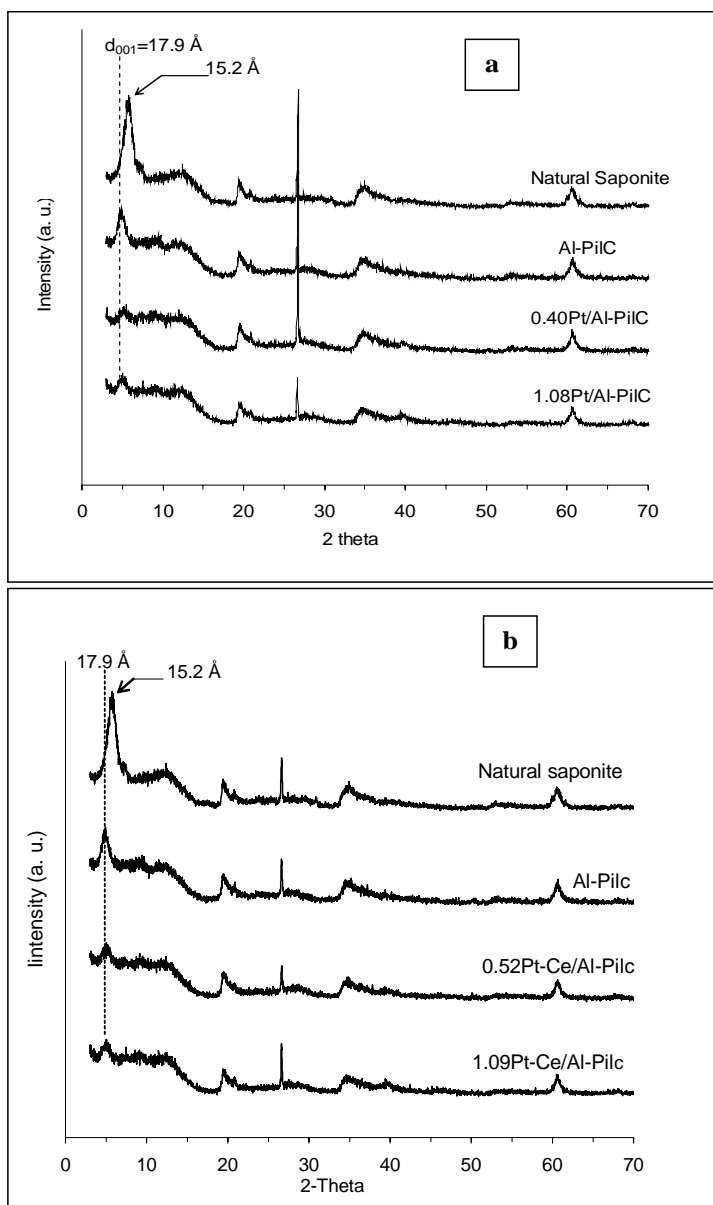

Figure 1. X- ray diffraction patterns of the natural clay (not calcined), the pillared clay and the solid modified with Pt (a) and Pt-Ce (b).

Solid	d_{001}(Å)	V_{pG} (cm^{3}g^{-1})	V_{mpt} (cm^{3}g^{-1})	S_{BET}=S_{ext} (m^{2}g^{-1})	S_{mp} (m^{2}g^{-1})	S_{total} (m^{2}g^{-1})
Natural saponite	15.2	0.145	0.008	109	22	131
Al-PilC	17.9	0.229	0.042	127	119	246
0.4Pt/Al-PilC	17.3	0.184	0.024	100	68	168
1,08Pt/Al-PilC	17.2	0.142	0.011	64	31	95
0.52Pt-Ce/Al-PilC	17.2	0.225	0.048	100	136	236
1.09 Pt-Ce/Al-PilC	16.7	0.223	0.042	124	119	243

Table 1. Basal spacing (d_{001}) and the textural properties of the solids[*].

[*]V_{pG}: total pore volume by the Gurvitsch method (at P/P$_0$ =0.99). V_{mpt}: micropore volume by t-plots. S_{BET}: BET surface area (external) employing the Remy approach [13]. S_{mp}: micropore area determined by the t-plots method. S_{total}: total surface area.

solids prevents the damage of the textural properties, showing similar values of surface areas and pore volumes
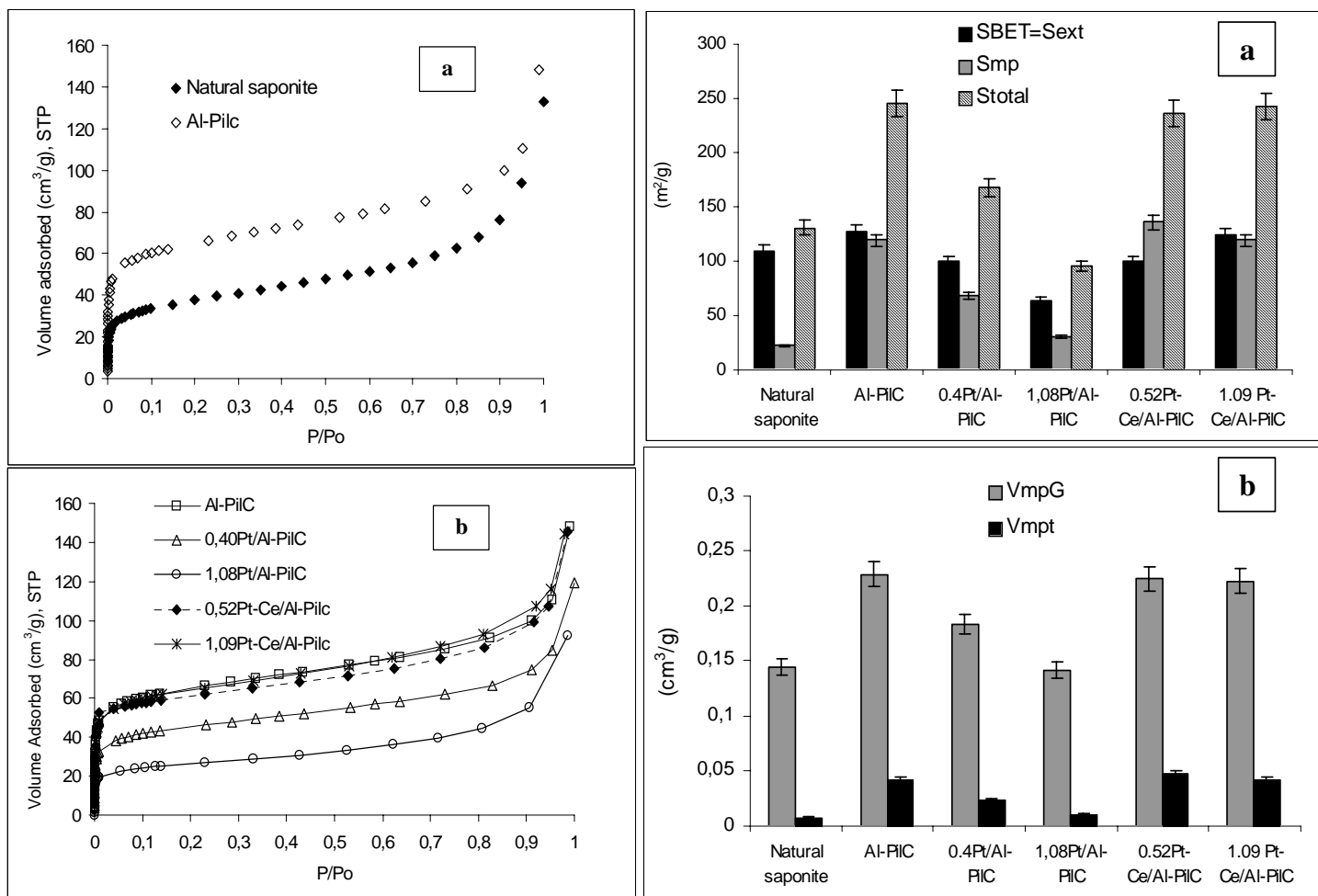
to those found for the alumina-pillared clay.

Figure 2. Nitrogen adsorption isotherms of the natural clay, the alumina-pillared clay and the solids based on Pt and Pt-Ce supported over the pillared clay.   Figure 3. Comparison

of the micropore areas (a) and pore volumes (b) as they were defined in table 1.

Probably, the deterioration of the textural properties is produced for the obstruction of the micropores in the solids, by the formation of platinum nanoparticles on the surface of the pillared clay. Three facts may support this hypothesis: 1) In principle, the values of micropore volumes and micropore areas decrease in more quantity (43% in the solid 0,4Pt/Al-Pilc and 74% in the solid 1,08Pt/Al-Pilc) than the total volume of pore (20% in the solid 0,4Pt/Al-Pilc and 38% in the solid 1,08Pt/Al-Pilc) and that the external area (21% in the solid 0,4Pt/Al-Pilc and 50% in the solid 1,08Pt/Al-Pilc), respectively, taking as reference the values corresponding to the pillared clay (table 1). 2) Although the external surface areas can also be affected, no increase in this parameter was observed, which indicates that it is little probable that destruction of micropores with the consequent generation of mesopores and macropores can be occurred. 3) Addition of cerium prevents the loss of surface area (micropore area and external area) and micropore volume in the solids, which

can be a consequence of the recognized stabilizing effect of Ce to improve the metallic dispersion of Pt, controlling the growth of particles of the noble metal and preventing their agglomeration [17-19].

4. CONCLUSION

The impregnation of platinum on the pillared clay, without cerium incorporation, leads to deteriorate the textural properties of the pillared clay, probably due to the blockage of the solid micropores by formation of platinum nanoparticles. The cerium incorporation, before the platinum impregnation, constitutes a new way of synthesis that allows the conservation of initial microporosity from the pillared clay without negative effects on their structural feature. This way of synthesis (platinum impregnation with previous incorporation of cerium on the saponite-pillared clay) leads to the

obtaining of materials with structural and textural properties suitable to be employed as catalysts.

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