Effect of the Platinum Content on the Microstructure and Micropore Size Distribution of Pt/Alumina-Pillared Clays

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The aim of this work is to study the effect of the platinum content (0-1.8 wt % Pt) on the microstructure of an alumina-pillared clay. For this purpose, the nitrogen physisorption data at -196 °C, the micropore size distributions of the supported platinum catalysts, and the hydrogen chemisorption results at 30 °C have been analyzed and compared. The preparation of the catalysts has modified the textural properties of the Alpillared clay support, giving rise to a loss of surface area and micropore volume. After reduction at 420 °C, the presence of dispersed metallic platinum with mean crystallite size in the 22–55 Å range has been found by hydrogen adsorption. Comparison of all results reveals that the platinum species block the micropore entrances by steric hindrance to nitrogen access as the platinum content increases.

1. Introduction

The development in the 1970s of inorganic pillared interlayered clays (in short PILCs), an important category of microporous materials, has created remarkable new opportunities in the field of the synthesis and applications of clay-based solids.1-5 Materials with larger pore sizes and stronger acid properties than zeolites have been the object of this research. These materials are prepared by exchanging the chargecompensating cations present in the interlamellar space of the swelling smectitic clays with hydroxy-metal polycations. When the smectite clays are dispersed in water, the layers swell because of the hydration of the interlamellar cations which act as counterions to balance the negative charges of clay layers. Therefore, polyoxocations in aqueous solutions can be intercalated into the interlayer space by cation exchange. On calcining, the inserted polycations yield rigid, thermally stable oxide species, named pillars, which prop apart the clay layers and prevent their collapse. This process results in an interesting twodimensional porous structure of molecular dimensions.

Compared to other microporous solids, pillared clays have several advantages. First, clays are abundant natural materials, and pillared clays are synthesized under conditions milder than those of the synthesis of aerogels, heteropolyoxometalates, and zeolites.⁶ Another feature is that pillared clays have pore openings of about 10 Å, larger than those of zeolites and activated carbons, that facilitate the incorporation of metal ions, either at the stage of pillar formation or in the postpillaring treatment.³ Thus, pillared clays have a potential to be used as molecular sieves and shape-selective catalysts for a wide range of molecular sizes.

The microporous structure of the pillared clays is characterized by the interlayer spacing, which is the distance between the clay layers, and the interpillar spacing, which is the distance between the intercalating species. These spacings can be controlled to a great extent by adjusting the various parameters involved in the synthesis process.⁷ The incorporation of specific cations into the pillared structure can improve the adsorption and catalysis properties of the final pillared solids.

Several authors have reported various techniques of doping pillared clays with controlled amounts of cations without causing significant damages to the layered structures,^{8–10} although the micropore structure and surface nature of the solids are altered by the introduced cations, this resulting in a significant modification in adsorption properties of the doped clays.¹¹ The microstructure developed in the pillaring process, in particular the micropore size distribution (MPSD), determines and limits the potential use of pillared clays in catalytic, purification, and sorption-based separation processes. Therefore, the characterization and quantitative evaluation of the microstructure is the object of a considerable research effort,^{12–20} with experimental and theoretical studies based on gas adsorption being the approach most widely considered.

Malla and Komarneni²¹ improved the water adsorption properties of pillared clays by introducing Ca²⁺ into the interlayer spacing. Molinard and Vansant²² showed N₂/O₂ selectivities by cation-modified pillared clays with ionexchanged alkaline earth ions and reported no adsorption for N₂ and O₂ at room temperature. Cheng and Yang²³ also studied the N₂ and O₂ adsorption capacities of alkali metal ionexchanged pillared clays showing for Li⁺/Zr-PILC better results than those obtained by Molinard and Vansant. The incorporation of different-sized charge-compensating alkali and alkaline-earth cations into the structure of pillared clays has been examined by Hutson et al.,¹¹ finding only a change in the pore volumes and a corresponding shift in the percentage of total micropore

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volume from the micropores and supermicropores to the ultramicropores. Zhu et al.²⁴ studied the effect of heat treatments on the pore and adsorption characteristics of sodium-doped Al-PILCs. They observed that the adsorption capacity is clearly related to the cation content and the calcination temperature. Recently, the modification of the textural properties of Al-, Zr-, and Ti-PILCs upon doping with copper has been investigated by Bahranowski et al.,²⁵ indicating that the effect of the copper addition on the texture of pillared matrices depends on the nature of pillars and on the method of doping, affecting the micropore and the mesopore systems.

Platinum-supported catalysts have been widely studied and used in various applications, alumina being the most used support and several compounds being employed as source of the metal. We have recently reported the incorporation of platinum into pillared clavs by means of impregnation with [PtII-(NH₃)₄]Cl₂, the resulting solids being used in the complete oxidation of acetone and methylethyl ketone, two important volatile organic compounds (VOCs).^{26,27} Another interesting coordination compound of platinum which can be used as precursor is [Pt^{II}(acac)₂], acac being an acetylacetonate ligand, having the advantage that only organic moieties are bonded to platinum in the coordination compound, giving a good dispersion of platinum on the surface of the pillared clay.²⁸ Thus, the aim of this work is to contribute to the evaluation of the microstructure developed by an alumina-pillared clay used as support of platinum for the catalytic combustion of CO.

2. Experimental Section

The natural clay mineral used in this work was a saponite from Yunclillos deposit (Toledo, Spain). The fraction with particle size smaller than 2 μ m was obtained by aqueous decantation of the natural clay and used for the intercalation experiments.

An aluminum polycation solution^{29,30} was prepared by slow addition of a 0.1 mol/dm³ solution of Al(NO₃)₃•9H₂O (Merck, 95.0%) to a 0.2 mol/dm³ solution of NaOH (Merck, 99.0%) under vigorous stirring, with an OH⁻/Al³⁺ mole ratio equal to 2.4 (pH = 4.0). The hydrolyzed solution was allowed to age for 48 h at 40 °C under continuous stirring. An Al/clay ratio of 6.6 mmol/g was used in the intercalation process. The clay suspensions were kept in contact with the solution at 40 °C for 2.5 h, washed by centrifugation and dialysis until absence of chloride, dried at 80 °C for 4 h, and calcined at 500 °C for 2 h.

X-ray powder diffraction (XRD) patterns of the solid were obtained using a Philips PWO 1150/90 diffractometer with Ni-filtered Cu K α radiation.

Supported platinum catalysts were prepared by wet impregnation of the alumina-pillared clay with a solution of platinum-(II) acetylacetonate ($Pt(C_5H_7O_2)_2$, Aldrich, 97%) in dioxane (Merck, 99.5%). The resulting slurries were evaporated slowly under reduced pressure in a rotavapor, and the obtained solids were calcined in air at 500 °C for 5 h to give the Pt/Al-PILC catalysts. The platinum content was determined by atomic absorption spectroscopy using a Varian spectrophotometer model A10. The samples will be referred to in wt %-Pt/Al-PILC notation.

Nitrogen (Agafano-Colombian, 99.9990%) physisorption experiments were performed at -196 °C using a Quantachrome Autosorb-1-MP adsorption analyzer. The samples were previously degassed at 300 °C for 12 h at a pressure lower than 50 μ mHg. The weight of each sample was 0.2 g. Only the nitrogen adsorption data up to a relative pressure of 0.2 were taken into account for the micropore characterization.



Figure 1. Nitrogen adsorption at -196 °C, in a semilogarithmic plot, starting from low pressures: (\bigcirc) Al-PILC, (\square) 0.4-Pt/Al-PILC, (\diamondsuit) 1.1-Pt/Al-PILC, (\bigtriangleup) 1.8-Pt/Al-PILC.

Hydrogen (Agafano-Colombian, 99.90%) chemisorption experiments were performed at 30 °C by a dynamic pulse method using a Quantachrome ChemBET-3000 TPR/TPD. The samples were reduced at 420 °C, then purged with argon (Agafano-Colombian, 99.90%) for 0.2 h at 420 °C, and finally cooled to room temperature under an argon flow. Hydrogen pulses were injected at 30 °C until the area of consecutive eluted pulses was constant.

3. Results and Discussion

The basal spacings of the parent saponite and of its pillared modification with alumina, determined by XRD analysis, are 15.2 and 17.9 Å, respectively.

The study of the surface and the porous network of the pillared clays using nitrogen adsorption data can provide useful information about the location of the impregnated cations. The nitrogen adsorption of the support and of the impregnated solids starting from low pressures is shown in Figure 1, where it can be seen that the adsorption isotherms of Al-PILC and 0.4-Pt/ Al-PILC were of type I in the Brunauer, Deming, Deming and Teller (BDDT) classification,³¹ while the adsorption isotherms of the rest of samples were of type II. The textural properties are presented in Table 1. The Langmuir surface area (SLang) was calculated from adsorption data in the relative pressure range between 0.01 and 0.05, considering a nitrogen molecule crosssectional area of 0.160 nm².³¹ The total pore volume (V_p) was assessed from the amount of nitrogen adsorbed at a relative pressure of 0.99, assuming that the density of the nitrogen condensed in the pores is equal to that of liquid nitrogen at -196 °C (0.81 g/cm³).³¹ The cumulative mesopore volume $(\Sigma V_{\rm p})$ was determined for pores in the range between 15 and 500 Å using the Barrett–Joyner–Halenda (BJH) method.³¹ The surface area of the samples varied between 92 and 253 m^2/g and their pore volumes between 0.142 and 0.229 cm³/g, depending on the platinum content (see Table 1).

Several methods and models have been applied to the nitrogen adsorption data for various pore geometries in order to characterize the microporosity of the solids.^{19,32} In the present work, the micropore size distributions (MPSD) derived from the models proposed by Horvath and Kawazoe³³ (HK), Cheng and Yang¹⁴ (ChY), and Saito and Foley³⁴ (SF) have been used to study the microporous region of the solids. The physico-chemical properties of the adsorbate—adsorbent system required

TABLE 1: Textural and Metallic Properties Derived from Nitrogen Adsorption at -196 °C and Hydrogen Adsorption at 30 °C

sample	S_{Lang}^{a} (m ² /g)	$S_{\rm ext}^{b}$ (m ² /g)	$V_{\rm p}{}^{c}~({\rm cm}^{3}/{\rm g})$	$\sum V_{\rm p}^{d}$ (cm ³ /g)	$S_{\rm Met}^{e}$ (m ² /g)	$D_{\mathrm{Pt}}^{f}(\%)$	$d_{\mathrm{Pt}^g}(\mathrm{\AA})$
Al-PILC	253 ($K^h = 486$)	47	0.229	0.112			
0.4-Pt/Al-PILC	175 (K = 468)	38	0.184	0.065	0.502	48.3	22.3
1.1-Pt/Al-PILC	103 (K = 462)	45	0.142	0.102	0.547	19.5	55.2
1.8-Pt/Al-PILC	92 ($K = 453$)	48	0.158	0.105	0.991	21.3	50.5

^{*a*} Specific surface areas from the Langmuir equation ($0.01 \le p/p^{\circ} \le 0.05$, interval of relative pressure). ^{*b*} Specific external surface areas obtained from the *t*-plot method. ^{*c*} Specific total pore volumes at $p/p^{\circ} = 0.99$. ^{*d*} Cumulative pore volumes from the Barrett–Joyner–Halenda (BJH) method (for pores in the 15–500 Å range). ^{*e*} Metal surface area. ^{*f*} Platinum dispersion. ^{*g*} Mean size of the platinum particles. ^{*h*} Langmuir *K* values, characteristic of the intensity of the adsorbate–adsorbent interactions.



Figure 2. Micropore size distributions derived from the Horvath–Kawazoe model: (\bigcirc) Al-PILC, (\square) 0.4-Pt/Al-PILC, (\diamondsuit) 1.1-Pt/Al-PILC, (\bigtriangleup) 1.8-Pt/Al-PILC.



Figure 3. Micropore size distributions derived from the Cheng–Yang model: (\bigcirc) Al-PILC, (\square) 0.4-Pt/Al-PILC, (\diamondsuit) 1.1-Pt/Al-PILC, (\bigtriangleup) 1.8-Pt/Al-PILC.

by these models were estimated as proposed by Gil and Grange.¹⁶ The MPSD obtained in this way are shown in Figures 2-4. As can be seen, the distributions are bimodal and do not depend a lot on the particular model. It seems that the microstructure of these materials can be equally described by either slitlike or cylindrical pore geometries when nitrogen is used as adsorbate.¹⁹ When the MPSD of the various samples are compared, no differences are observed. The distributions show a first maximum at about 4.9 Å and a second maximum at 6.4 Å. The pore diameter ranges of the second maximum of the distributions are summarized in Table 2.

The micropore volumes ($V_{\mu p(HK)}$), calculated according to the HK model and the method proposed by Gil and Grange,¹⁶ are



Figure 4. Micropore size distributions derived from the Saito–Foley model: (\bigcirc) Al-PILC, (\square) 0.4-Pt/Al-PILC, (\diamondsuit) 1.1-Pt/Al-PILC, (\triangle) 1.8-Pt/Al-PILC.

summarized in Table 2. For comparison purposes, the micropore volumes have been calculated by means of the Dubinin–Astakhov (DA) equation³⁵ in the relative pressure range between 0.01 and 0.05 ($V_{\mu p(DA)}$), and the results are also included in Table 2.

When the results of the Al-PILC and the platinum-doped materials are compared, a continuous decrease of the adsorbed nitrogen volume is observed for the supported solids in the whole relative pressure range. This fact shows that the impregnation with platinum produces a continuous loss of the textural properties of the Al-PILC as the Pt content increases up to 1.1 wt %. The textural properties remain almost unchanged when the platinum content increases from 1.1 to 1.8 wt % (see Table 1). If the specific mesopore volume is estimated by subtracting the micropore volume from the total pore volume, it is revealed that the mesopore volume remained almost unchanged and that the pore volume loss suffered by the materials almost exclusively affected the micropores of the Al-PILC. This suggests that some platinum species may block the entrance to the porous network and/or occupy the inner pores of Al-PILC during the preparation process.

It has been reported that the structural heterogeneities of materials, which can arise from networking effects related to interconnected pores of various sizes and shapes, can be described by the fractal geometry from theoretical and experimental studies of adsorption. The fractal dimension, which quantitatively evaluates the fractal geometry,³⁶ is considered as a measure of the surface and structural irregularities of a solid. The value of this dimension can vary from 2 to 3,³⁷ the lower limiting value of 2 corresponding to a perfectly regular smooth surface, whereas the upper limiting value of 3 is related to the maximum allowed complexity of the surface. The fractal dimensions (D_F) of the solids calculated by the method proposed

TABLE 2: Microporous Properties Derived from Nitrogen Adsorption at - 196 °C

	slitlike model			DA equation			
sample	$V_{\mu p(\mathrm{HK})}^{a} (\mathrm{cm}^{3}/\mathrm{g})$	$d_{\mathrm{pHK}}{}^{b}$ (Å)	$d_{\mathrm{pChY}^c}(\mathrm{\AA})$	$V_{\mu p(\mathrm{DA})}^{d} (\mathrm{cm}^{3}/\mathrm{g})$	E^e (kJ/mol)	n ^f	$D_{\mathrm{F}}{}^{g}$
Al-PILC 0.4-Pt/Al-PILC 1.1-Pt/Al-PILC 1.8-Pt/Al-PILC	0.103 0.072 0.042 0.038	5.5-12.5 5.4-12.6 5.5-12.5 5.5-12.3	5.5 - 9.9 5.3 - 10.4 5.5 - 10.7 5.5 - 10.2	0.097 0.069 0.035 0.035	19.2 19.8 13.7 19.7	2.2 1.9 6.7 2.1	2.79 2.77 2.76 2.74

^{*a*} Specific micropore volumes derived from the Horvath–Kawazoe (HK) model. ^{*b*} Pore diameter range of the second maximum of the Horvath–Kawazoe micropore size distributions. ^{*c*} Pore diameter range of the second maximum of the Cheng–Yang micropore size distributions. ^{*d*} Specific micropore volumes derived from the Dubinin–Astakhov (DA) equation. ^{*e*} Characteristic energy from the Dubinin–Astakhov equation. ^{*f*} Exponent of the Dubinin–Astakhov equation. ^{*s*} Fractal dimensions calculated from Avnir-Jaroniec method in the relative pressure range 0.08–0.2.

by Avnir and Jaroniec³⁸ in the range of relative pressures between 0.08 and 0.2^{39} are included in Table 2. The values obtained for the materials of this study, 2.74-2.79, are close to the upper limiting value of 3, thus indicating a high heterogeneity of the solids, caused by structural and/or surface factors.

All the D_F values are very similar, suggesting a high structural similarity of the solids. The fractal dimension is estimated from the adsorption data in the range of relative pressures 0.08-0.2 where the total micropore filling takes place and only the supermicropores are characterized. More information about the structural heterogeneity of the materials can be obtained from the MPSD, the specific micropore volumes, and the *n* exponent of the Dubinin-Astakhov equation. The comparison of the specific micropore volumes and of the *n* exponents, also given in Table 2, suggests that there is a substantial portion of micropores with steric hindrance for the accessibility of nitrogen in the samples 1.1-Pt/Al-PILC and 1.8-Pt/Al-PILC. In the case of the sample 1.1-Pt/Al-PILC, this loss of accessibility can be due to the presence of platinum species that block the pore entrances generating fine pores, as indicates the high value of *n*. An increase of the platinum content, sample 1.8-Pt/Al–PILC, reduces the accessibility to the fine pores, diminishing the value of *n*.

The measurement of the metallic surface of the platinum pillared clays using hydrogen adsorption data provides information about the location of the impregnated cations. The catalyst properties related to the metal phase are shown in Table 1. The metal dispersion, $D_{\rm Pt}$, was calculated from the chemisorption results using the formula D(%) = 0.039U/W, where U is the *µ*mol of gas chemisorbed per gram of catalyst and *W* the metal weight fraction, assuming a stoichiometry of one hydrogen molecule adsorbed per two surface platinum atoms.^{40,41} An average cross section area per surface platinum atom of 8.41 Å², as proposed by Lemaitre et al.,⁴¹ has been used for the calculation of the metal surface area, S_{Met}. The mean surface particle size was calculated from the metal dispersion values, assuming that the metallic particles on the surface of the catalysts are spherical and wholly exposed to adsorption⁴² and that the density of platinum is equal to 21.45 g/cm³.41 The metal surface area of the samples varied between 0.502 and 0.991 m^2/g and the mean particle size between 22.3 and 55.2 Å, depending on the platinum content (see Table 1).

The evolution of the platinum surface area and particle size confirm the textural properties obtained from nitrogen adsorption. As the platinum content increases, the microporous network is affected by blockage, and an effective reduction of the textural properties of the doped alumina-pillared clay is found. The platinum particle size reported in Table 1 is an average value corresponding to a more or less broad distribution. The mean platinum diameter calculated from hydrogen chemisorption indicates that some platinum species may occupy the microporous network of the alumina-pillared clay after the catalyst preparation process.

4. Conclusions

The platinum doping produces a continuous loss of the textural properties of the alumina-pillared clay, as a function of the quantity of the metal. This effect can have a strong influence on the accessibility of the molecules of adsorbates and reactants to active sites in the micropores when the solids are used as adsorbents or catalysts. The variation of the accessibility with the metal content can be utilized to control or improve the performance of the solids for certain chemical reactions.

The results from nitrogen physisorption data at -196 °C indicate that the mesopore volume remains almost unchanged and that the pore volume loss suffered by the materials almost exclusively affected the micropores of the pillared clay. Several approaches have been considered and compared in order to characterize the microporous structure of the pillared clays. The results obtained suggest that some platinum species occupy the inner porous network of the alumina-pillared clay after the preparation process, blocking the pore entrances. The complexity of these materials is confirmed by the structural analysis from the fractal dimension.

The metal properties evaluated by hydrogen chemisorption at 30 °C and after reduction of the Pt/Al-pillared saponite at 420 °C can also explain the textural properties obtained from nitrogen adsorption.

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