

PREPARATION OF PLATINUM CATALYSTS BASED ON PILLARED CLAYS

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Abstract

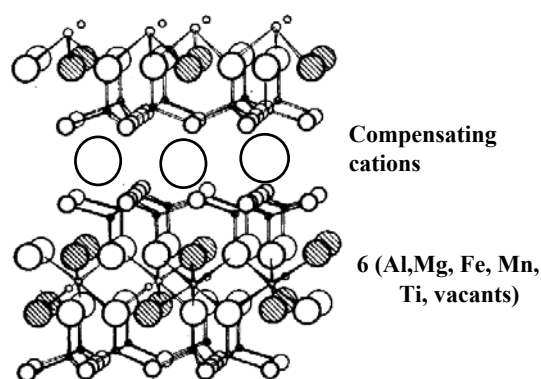
Four clays (two saponites, one montmorillonite and one hectorite) were intercalated with the "classic" Al₁₃ Keggin polycation, and one of the saponites also with a new Al polycation containing an organic moiety. The intercalated solids, after stabilization by calcination, were used as supports for the preparation of Pt impregnated catalysts. The intercalation with the new Al-polycations, the characterization of the Pt supported catalysts, the mechanism of the interaction between the Pt precursor and the support surface, and the activity of the catalysts for a hydrogenation reaction are discussed in this paper [1].

1 INTRODUCTION

Clay minerals have been used by humanity since Antiquity. In fact, pottery was one of the first "industrial" human activities. Now, clays are greatly used in paper coating, ceramics, paint, plastics, rubber or cracking catalysts. These utilisations are strongly determined by the properties of the clays. Thus, in some cases, chemical modification of these properties is carried out before a given use, e.g., the clays employed as cracking catalysts in the petrochemical industry are previously submitted to acid activation. Nowadays, the use of clay materials in new and very specific applications is being considered, such as in Fine Chemistry. For that, very specific modifications of the clay properties are needed, which design the properties of the final solids, what is usually called Molecular Engineering. Pillaring is one of the most developed procedures of Molecular Engineering of layered smectitic clays.

Pillared clays, which have been greatly studied in recent years, are prepared by a soft-chemistry process based on the substitution of the interlayer cations of a smectitic clay by bulk inorganic polycations, followed by a thermal stabilization of the precursor obtained in the first step. The smectites are 2:1 clays, composed of one octahedral layer sandwiched between two tetrahedral layers. Their structure is shown in Scheme I, and their general formula is [Si_{8-x}Al_x] [(Al, Mg, Fe, Ti, Mn)_yO₂₀(OH)₄[M_z]]. The tetrahedral sheet presents a partial isomorphic substitution of Si by Al, while different cations may be present in the octahedral sheet. Both the substitution in the tetrahedral sheet, and the substitutions and vacant positions in the octahedral one give rise to negative charge in the layer. This charge is balanced by the compensating cations, denoted as "M" in the formula

and located between the sheets, allowing them to swell in the presence of appropriate chemical species. The different smectites differ in the percentage of Si-Al substitution in the tetrahedral sheet, in the chemical composition of the octahedral sheet (mainly aluminic or magnesian), and in the nature of the compensating cations.



Scheme I: General structure of smectitic clays.

The intercalation of different smectitic clays has been studied, mainly of montmorillonite (aluminic smectite whose charge is mainly located in the octahedral sheet), saponite (magnesian smectite with tetrahedral charge) and hectorite (magnesian smectite with octahedral charge). Different polycations have been employed as intercalating species, based on Al³⁺, Si⁴⁺, Ti⁴⁺, Zr⁴⁺, Cr³⁺, Fe³⁺ or Ga³⁺, the most used and best known being the polycation [Al₁₃O₄(OH)₂₄(H₂O)₁₂]⁷⁺, usually denoted as Al₁₃ Keggin. The whole process is somewhat long and laborious, because of the successive intercalation, washing (centrifugation or dialysis), and calcination steps, and because it implies the handling of large volumes of clay suspensions and of intercalating solutions. The final solids, although they have layered structure with large basal spacing, a well defined porous structure, high surface area, good thermal stability and acidic nature, are used as adsorbents or catalysts, their main potential uses, in a moderately high extension. Their use is appropriate for very specific processes, in which the specificity of the application compensates the large synthetic process [2].

One of the ways for functionalizing these solids is their use as catalyst supports, the pillared clays being impregnated with active phases of transition or noble

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metals. The excellent surface properties of pillared clays make them promising supports in the preparation of highly selective catalysts, and some papers have already been published in recent years describing the preparation of catalysts of Pt, Rh, V or Cu, among other elements, supported on pillared clays [2]. In the present paper, we report on the results of the research carried out under two TMR Marie Curie Grants, focused on the preparation of clays pillared with a new Al-polycation, recently described in the solution chemistry of this element and, in a second step, the use of these new pillared clays and of Al₁₃-Keggin pillared clays as supports for the preparation of Pt catalysts.

2 EXPERIMENTAL

Two saponites, one montmorillonite and one hectorite were used as starting materials: the saponites from Ballarat (California, USA) and Yuncillos (Toledo, Spain), the montmorillonite from Cheto (Arizona, USA), and the hectorite from San Bernadino (California, USA), using in all cases the ≤ 2 μm fractions, obtained by aqueous dispersion and decantation. The clays were pillared with Keggin Al₁₃ polycations, and in the case of Ballarat saponite also with "Al₁₃-heidi" polycations ("heidi" = hydroxyethyliminodiacetate ligand). The first one is synthesized by hydrolysis of AlCl₃·6H₂O with 1M NaOH. A ratio OH⁻/Al³⁺=2.2 was used for the synthesis of the polycations, and Al³⁺/clay=5 mmol/g in the intercalating reaction. The second polycation was prepared by the reaction of AlCl₃·6H₂O and hydroxyethyliminodiacetic acid, adjusting to pH=5.0 with NaOH. Al/heidi ratios = 2 and 3 were used in the preparation of the polycations, and Al/clay ratios = 5, 10 and 20 mmol/g in the intercalation reaction. The fresh clay-intercalating solution suspensions were stirred for 24 hours, centrifuged and washed by dialysis with distilled water until absence of chloride anions, thus giving the intercalated solids. Calcination at 500°C for 4 hours (air flow; heating rate of 1°C/min) gave the pillared solids.

The Pt catalysts were prepared by wet impregnation of the pillared clays with [Pt(NH₃)₄]Cl₂ solutions, using an amount equivalent to a final Pt content in the catalysts of 2.3 wt %, followed by drying in a rotary evaporator. A reference Pt/Al₂O₃ catalyst was prepared by impregnation of a commercial γ -alumina sample (γ -alumina is one of the forms of anhydrous Al₂O₃ in which the crystal structure is regarded as a spinel structure with cationic vacancies). More details about the synthesis may be found in our previous papers on this subject [1].

Elemental analyses of the solids were carried out by the Central Analysis Service of the CNRS (Vernaison, France). X-ray powder diffraction (XRD) was carried out by using a Siemens D-5000 diffractometer, employing Cu K α filtered radiation. Specific surface areas were estimated by the Brunauer-Emmett-Teller (BET) treatment of nitrogen adsorption data, obtained from a

Quantasorb Junior apparatus. FT-IR spectra were recorded on a Bruker IFS 66V spectrometer, using the KBr pellet technique. The study in the Near Infrared (NIR) region was carried out in reflectance mode using a Cary 5 spectrometer (900-2500 nm). This equipment was also used for studying the samples in the UV-Vis region (190-900 nm). Temperature-Programmed Reduction (TPR) was carried out in a quartz gas flow reactor, under a stream of 5% v/v H₂ in Ar at atmospheric pressure, measuring the hydrogen consumption by a Thermal Conductivity Detector (TCD). Thermal analyses were performed on a Seiko SSC 5200H thermal analyzer. High Resolution Transmission Electronic Microscopy (HR-TEM) was carried out by using a JEOL 100 CXII UHR equipment. Finally, the catalytic activity of the samples was studied for the reaction of hydrogenation of benzene, carried out at 50°C and atmospheric pressure in a tubular fixed-bed reactor. Prior to the reaction, the catalysts were activated by reduction in flowing hydrogen at 350°C.

3 RESULTS AND DISCUSSION

3.1 Intercalating solutions

The hydrolysis of AlCl₃·6H₂O with NaOH easily leads to the formation of the Al₁₃ Keggin polycation, well defined in the literature [3,4]. The polycation formed in the Al³⁺-heidi system has the formula [Al₁₃(μ_3 -OH)₆(μ_2 -OH)₁₂(heidi)₆(H₂O)₆]³⁺, for its synthesis we have followed the procedure described by Moore et al. [5,6], using Al/heidi ratios = 2.0 and 3.0 (Al/heidi molar ratio in the polycation is 2.17). ²⁷Al Nuclear Magnetic Resonance (NMR) spectroscopy allowed us to confirm the formation of this polycation, because of the signals at 10 ppm (characteristic of Al cations in the central core of the oligomer), and at +25 ppm (characteristic of Al cations in the shell of the structure).

3.2 Intercalated and pillared solids

The intercalation of the polycations in the interlayer galleries of the clays was successful in all cases. When intercalating with Al₁₃ solutions, the basal spacing of the clays, *d*, increased from the values in the natural clays (close to 14Å) to values between 17.9 - 20.3Å. The calcination of these solids at 500°C, usual procedure for the stabilization of solids intercalated in this way, led to solids with *d*=16.9-18.2Å, except for San Bernadino hectorite, whose structure collapsed at this temperature, hence it was calcined at 400°C (*d*=18.4Å). The intercalated solids were clearly better ordered than the parent clays. When calcining them a small loss of ordering was observed.

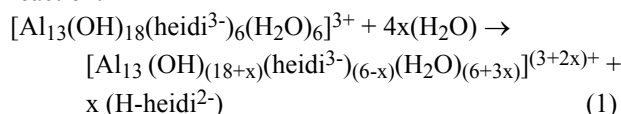
The solids intercalated with Al₁₃-heidi solutions showed larger basal spacings, between 23.1-25.3Å. The optimal intercalation with this bulky polycation led to large basal spacings, but the XRD showed poor

crystallinity, with peaks sometimes broader and less intense than in the parent Ballarat saponite (very crystalline itself). This suggested the presence of layers intercalated with different polycations, or an irregular stacking of intercalated and non-intercalated layers. Their calcination at 500°C made *d* decrease to values of 15.0-16.9Å, with a small decrease in their crystallinity. The heidi ligands situated in the peripheral octahedra of the polycations were burned off by calcination, causing the decrease in *d*. But this elimination produced the opening of the interlayer galleries of the solids, producing the strong increase observed in the surface area of the pillared solids.

The intercalated solids fixed variable amounts of Al, which implied different densities of pillars. In the solids intercalated with Al₁₃, the amount of Al fixed varied between 4.3-5.3%, while in the Al₁₃-heidi series, the amount fixed increased up to 10.3%. This fact is related to the charge of the polycations, the Al₁₃ unit has a charge of +7 and the Al₁₃-heidi unit of +3, so in the second case a higher number of polycations is needed to compensate the same layer charge. The presence of C and N in the Al₁₃-heidi intercalated solids confirmed the fixation of heidi ligands. The N/C ratio in the solids was close to that in the theoretical formula of the polycation, suggesting that the structure of the polycations did not drastically change when intercalated between the layers of the clay. This was verified by the ²⁷Al NMR spectra of the intercalated solids, especially by means of the presence of a peak at +24 ppm, characteristic of the Al octahedra in the shell of the polycations. Also IR spectra showed the bands characteristic of the heidi ligands: bending vibrations of C-H groups at 1395 cm⁻¹ and stretching vibration of C-H at 3000-3250 cm⁻¹. Moreover, the C/Al and N/Al ratios were lower in the solids than in the polycation, which may be due to the fixation of Al as other species, oligomeric or simple, different from Al₁₃-heidi.

The number of polycations fixed led to a high density of 0.11 Al₁₃-heidi oligomers per unit cell (the maximum density permitted by steric constraints when intercalating Al₁₃-polycations has been calculated to be 0.17 oligomers per unit cell, and Al₁₃-heidi polycations are larger than the Al₁₃). The amount of Al₁₃-heidi fixed, if they maintain in the solids the 3+ charge they have in solution, was not enough to compensate the substitutional charge. Thus, other Al species, with a lower polymerization degree and/or higher charge than Al₁₃-heidi units, may participate in the cation exchange reaction (this is the case of [Al(H₂O)₆]³⁺, [Al(H₂O)₅(OH)]²⁺, or [Al₂(H₂O)₈(OH)₂]⁴⁺). This is not very probable due to the very strong affinity of the tetradentate heidi ligands for Al³⁺ cations [6]. ²⁷Al NMR of the intercalated solids allowed us to confirm the absence of such species by the absence of any peak close to 0 ppm. Thus, the compensation of the charge may be explained by a

hydrolysis reaction in the Al₁₃-heidi units that increases their individual charge. We propose the following reaction:



However, the value of *x* necessary to justify the charge compensation by this mechanism did not satisfactorily fit with C and N analyses.

The Al₁₃-intercalated solids had BET surface areas between 303-372 m²/g for saponites and montmorillonite, in the range usually reported for alumina pillared clays. The hectorite intercalated solid showed a lower surface area, 208 m²/g, even though this solid was calcined at a lower temperature, 400°C. The Al₁₃-heidi intercalated solids all had surface areas close to 25 m²/g, which was the external surface of clay layers. The calcination of these solids produced a strong increase in the surface area, up to 207-353 m²/g. This suggested that Al₁₃-heidi units, although separating the layers to a large distance, filled the interlayer space in the intercalated solids, blocking the access to the internal porosity. When the organic moieties were eliminated by calcination, the porosity was opened, increasing the surface area of the solids.

Under calcination, the organic ligands disappeared, as confirmed by all the techniques. Thermal analyses showed a 7% weight loss between 300-380°C in the TG curve, with an associated exothermal effect in the DTA curve. The ²⁷Al NMR spectra of the pillared solids revealed the disappearance of the signals characteristic of the Al₁₃-oligomers and a clear reorganisation of the Al environment, with the formation of cross-linking between the clay layers and the pillars (Al_{sheet}-OH-Al_{pillar} bonds). The mechanism is similar to that accepted for Al₁₃-pillared clays [7,8], but more intense, the removal of heidi ligands by calcination makes the Al of the shell of Al₁₃-heidi polycations coordinately undersaturated and, consequently, makes it have a high reactivity to form chemical bonds with the layers of the clay, corroborated by the presence of a broad peak at +67.5 ppm in the ²⁷Al NMR spectra, assigned to inverted Al bonding tetrahedra.

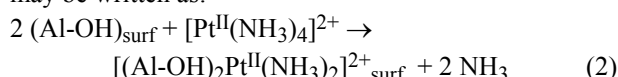
The solids impregnated with [Pt(NH₃)₄]Cl₂ maintained the layered structure, although with a small decrease in the basal spacing, as compared to the solids before impregnation. The surface area strongly decreased in this step, to values close to 25 m²/g, suggesting that the Pt-complexes are adsorbed on the surface of the pillars blocking the access to the internal porosity of the solids. The evolution of the X-ray diffraction patterns of the solids in different steps of the synthetic procedure is given in Figure 1.

The NIR spectra of the intercalated solids showed a band at 1389 nm, assigned to the overtone of the stretching vibration of structural OHs (2ν_{OH}), with a broad band at higher wavelengths (2ν_{OH} of adsorbed

water). The intensity of these bands decreased in the pillared samples, although without disappearing. The combination band ($\nu+\delta$)_{OH} of water appeared at 1907 nm, and the ($\nu+\delta$)_{OH} of structural OHs in the 2200-2400 nm range. The Al₁₃-heidi intercalated solids also showed a band of $2\nu_{\text{CH}}$ vibration, which appeared as a small shoulder at ≈ 1725 nm, and disappeared in the pillared solids, confirming the total elimination of heidi ligands at 500°C.

The Pt-impregnated solids, due to the organic ligands contained in the precursor, showed new bands. The overtone of N-H bonds ($2\nu_{\text{NH}}$) was observed at 1550 nm, clearly showing that NH₃ ligands remained in the solids, and had been not eliminated in the drying step. This band was present after calcination at 150°C but disappeared after 4 hours at 250°C. Thermal analyses under air showed a weight loss of $\approx 3\%$ at 310°C, with an exothermal effect, assigned to the elimination of NH₃ ligands. This process was observed at 310°C under thermogravimetric-differential thermal analyses (TGA-DTA) conditions, but the solids calcined at 250°C did not show NH₃ effects, due to the different experimental conditions employed, dynamic for TGA-DTA (heating rate 10°C/min), and static for the calcination.

supports from the spectra of the impregnated solids, thus showing a maximum at 308nm. The comparison with bibliographic data on Pt/SiO₂ and Pt/Al₂O₃ systems [9], suggested the formation of inner-sphere complexes in which part of the NH₃ ligands bonded to Pt^{II} are substituted in the coordination sphere by surface groups of the support. This was verified by a parallel experiment with [Pd^{II}(NH₃)₄]Cl₂, analogous to the Pt^{II} complex used, but Pd^{II} shows clear bands in the visible region. Thus, the interaction between the supports and the Pt^{II} complexes may be written as:



in which Al-OH are the surface groups of the aluminic pillars. This was in agreement with all experimental data, such as the maintenance of N-H stretching vibration bands of NH₃ after adsorption.

3.4 Pt^{II} reduction and electronic microscopy

The reduction of the Pt^{II} precursors is needed for the preparation of active catalysts based on metallic platinum, hence we have followed this process by TPR. The evolution was very different when solids prepared using

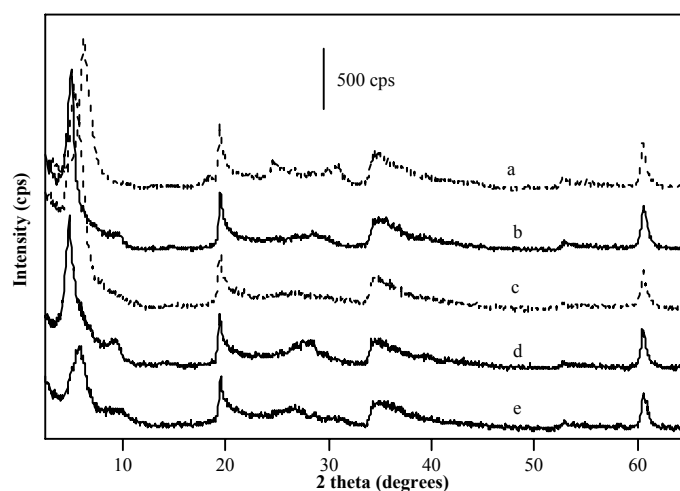


Figure 1. XRD patterns of natural Ballarat saponite (a); this clay pillared with Al₁₃ polycations (b); pillared with Al₁₃-heidi polycations, Al/heidi = 2, and Al/clay = 10 (c); sample b impregnated with [Pt(NH₃)₄]Cl₂ (d); and sample c impregnated with the same precursor (e).

3.3 Mechanism for the adsorption of the Pt precursor

The mechanism of the adsorption of Pt species is of particular interest, mainly for knowing whether they are adsorbed electrostatically or by forming outer-sphere or inner-sphere complexes with surface groups of the support. Pt^{II} does not show intense bands in the visible spectra and, in our samples, data on d-d transitions could only be obtained by subtracting the spectra of the pillared

Al₁₃ and Al₁₃-heidi pillared solids were used as supports (Figure 2). In the first case, Pt^{II} is reduced in a single and well-defined process at *ca.* 170 °C. At higher temperature, only a very small effect appeared, also observed in the TPR of the supports, and assigned to the reduction of octahedral cations of the clays (mainly Fe³⁺ → Fe²⁺). The solids prepared from Al₁₃-heidi pillared solids showed TPR curves with a wide reduction band between 150-300°C, which only sometimes could be resolved in two components at about 200 and 250°C.

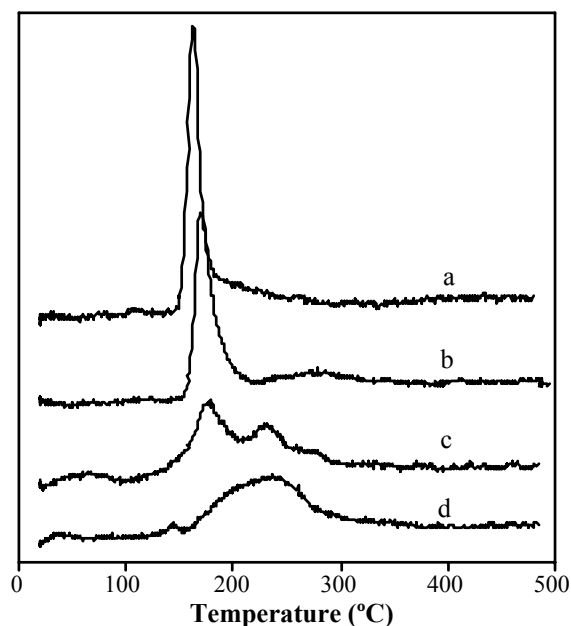
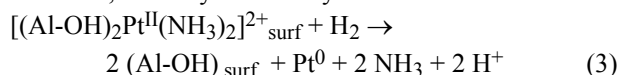


Figure 2. TPR curves of Pt-impregnated solids. Al₁₃ series: Ballarat saponite (a) and Cheto montmorillonite (b); and Al₁₃-heidi series: Al/heidi = 2 and Al/clay = 5 (c), and Al/heidi = 3 and Al/clay = 10 (d).

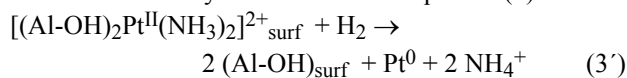
The TEM micrographs of the reduced solids derived from Al₁₃ series presented large Pt⁰ particles, showing a bimodal size distribution with maxima at *ca.* 100 and 200 Å. The shapes of the particles were unusual, not spherical or polyhedral but rather irregular. When studying the solids derived from Al₁₃-heidi series, a more homogeneous distribution was observed, with an average size of 40 Å, although particles as small as 8 Å were found. Thus, initially molecularly dispersed Pt(II) precursors have concentrated, at some stage in the reduction process, to form large particles, indicating substantial mobility. Such migration has also been observed in Pt/SiO₂ catalysts, explained by the existence of species [Pt(NH₃)₄(H₂)]^{x+} (“mobile hydrides”) [10], a similar species might exist in our Pt/pillared clays system.

The reduction of the Pt^{II} species to form metallic Pt by means of H₂ is influenced by the chemical environment of Pt(II) precursors in the impregnated solids. Assuming the formation of the inner-sphere complexes above indicated, one may reasonably write the reaction:

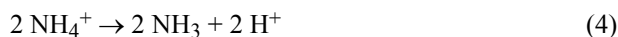


As ammonium ions can be retained in the solids as compensating cations of the clays, as has been previously

observed in a [Pt(NH₃)₄]²⁺-impregnated natural clay [11], a modification may be introduced in equation (3):



At higher temperature, NH₃ is evolved by the reaction:



This was verified by analyzing by Mass Spectrometry the gases evolved during the TPR experiment, which showed that NH₃ was released from the solids up to 100°C higher than the maximum in the reduction peak.

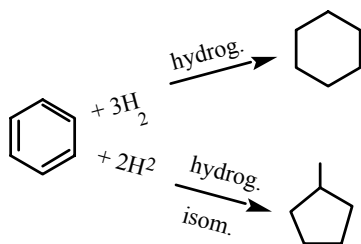
The theoretical H₂/Pt ratio deduced from the reduction reactions proposed is 1.0. But the integration of the TPR curves led to slightly lower ratios between 0.75 and 0.90. As in the conditions considered all Pt^{II} was reduced to Pt⁰, the low consumption of H₂ may be explained if one species in the solids can act as reducing agent, as is the case of NH₃. This mechanism was verified by calcining a Pt-impregnated solid under inert He atmosphere at 250°C, the XRD of the calcined solids clearly showed the presence of Pt⁰, undoubtedly confirming that NH₃ acted as reducing agent.

In the Al₁₃ series, the Pt^{II} complexes adsorbed on the surface of the pillars are distributed mostly in the internal porosity (*i.e.* the interlamellar space). The nucleation of the Pt⁰ particles upon reduction takes place between the clay layers, and due to steric hindrance the resulting particles are highly anisotropic. At the same time, their growth exerts considerable pressure both laterally (on the Al-containing pillars) and in the perpendicular direction (on the clay sheets), causing partial disruption of the microporous structure. In opposition, in the Al₁₃-heidi series, Pt⁰ nucleation occurs mostly on the external surface and therefore Pt particles grow unimpeded.

We have demonstrated that the access to the internal porosity is rather impeded in the Al₁₃-heidi series. This makes the Pt^{II}-complexes be adsorbed on the external part of the tactoids, and not in the interlayer region (or perhaps only to a very low extent). When the Pt^{II}-complexes are reduced, the nucleation and growth of the Pt⁰ particles occurs in the external region of the clay tactoids, the growth is not hindered by steric constraints, and the final Pt⁰ particles are more regular and the structure of the clay matrix is not disorganized.

3.5 Catalytic activity

The catalytic reaction is shown in Scheme II. If benzene is completely hydrogenated, cyclohexane is obtained; the parallel reaction involves a partial hydrogenation of the reagent, followed by an isomerization leading to the formation of methylcyclopentane (MCP).



Scheme II: Reaction routes for the hydrogenation of benzene.

Pt/Al₁₃-pillared clay supported catalysts were very active in the hydrogenation of benzene, converting 99-100% of the reagent, with a selectivity to cyclohexane close to 100%, and little deactivation. This behaviour was very similar for all the clays considered. Traces of MCP as a product of the reaction were detected for the samples prepared from Ballarat and Yuncillos saponites. The Pt/Al₁₃-heidi pillared clay catalysts converted 5-8% of the benzene feed, showing total selectivity to cyclohexane. On the other hand, the Pt/Al₂O₃ reference catalyst showed a conversion of 8%, with 100% selectivity to cyclohexane. Thus, the catalytic behaviour of Pt/Al₁₃-heidi catalysts was similar to that of the alumina-based catalyst, while the catalysts of the Pt/Al₁₃ series showed much higher conversions.

The different evolution of Pt-species also explained the activity of the final catalysts. The fact that in the Al₁₃-heidi series the Pt complexes were adsorbed only on the external surface of the tactoids, together with the form and size of Pt⁰ particles in this series made these catalysts show an activity similar to that of the Pt/Al₂O₃ catalyst. In the Al₁₃ series, the benzene hydrogenation activity was much higher, close to 100%, which we explain by the existence of acidic centres very close to the reduction sites, described in the bibliography for other supports [12,13]. In these positions, the benzene molecules are adsorbed on the acidic sites, and then react with the hydrogen atoms adsorbed on the surface of the nearby Pt particles, thus highly exalting the hydrogenation activity of the catalysts. Such bifunctional positions are created in the regions where the growth of Pt particles disrupt the clay layers, in which the aluminic pillars, the clay layers and the Pt⁰ particles are in intimate contact, being easily accessible for the reactive molecules. The existence of acidic centres is confirmed by the formation of small quantities of MCP; the isomerization is catalyzed by the acid centres, but this reaction acquires no importance because the hydrogenation reaction is more favourable.

4 CONCLUSIONS AND PERSPECTIVES

This work reports on two main achievements: first, the synthesis of new Al-pillared clay systems and, secondly, the suitable use of pillared clays as catalytic supports, with a wide approach to the phenomena occurring during the preparation of Pt/pillared clay catalysts.

The use of an Al-polycation containing the organic ligand N-(2-hydroxyethyl)-iminodiacetate led to a versatile and reproducible method of synthesis of new Al-pillared clays. The intercalation of a saponite with this polycation resulted in solids with good structural organisation and large interlayer spacings. The structure of the oligomer was preserved in the intercalated solids. The organic ligands blocked the access to the internal porosity of the clay, but the stabilization of the structure by calcination at 500°C opened this porosity by removal of the organic ligands.

These pillared materials, together with clays pillared with Keggin Al₁₃ polycations, were impregnated with the platinum complex [Pt(NH₃)₄]Cl₂, precursor of active Pt⁰ catalysts. The mechanism of the interaction between the active phase and the surface of the pillared clay supports has been studied. The complexes were adsorbed on the surface by an inner sphere complex mechanism, and the subsequent evolution under H₂ reduction was different for Al₁₃ and Al₁₃-heidi series: in the first one, bifunctional catalysts were obtained by the creation of close redox and acidic centres, with a strong disruption of the clay structure; in the second series, bifunctional centres were not created because of diffusional limitations of the Pt complexes in the pillared clay network. While these latter catalysts had a hydrogenation activity, tested for benzene hydrogenation, similar to Pt/alumina solids, the catalysts derived from Al₁₃ series showed conversions close to 100% with total selectivity to cyclohexane.

The main perspective of this work is the use of the Pt/pillared clay catalysts here described for other reactions. In this respect, their behaviour in an important environmental reaction, the complete catalytic oxidation of acetone in air stream, has already been studied, in the framework of a collaboration derived from the TMR grants here reported [14].

5 ACKNOWLEDGEMENTS

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