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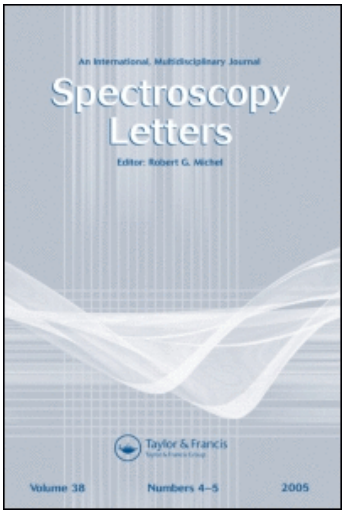

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

THE APPLICATION OF ELECTRON SPIN RESONANCE SPECTROSCOPY TO STUDIES ON COPPER(II) DOPED PILLARED CLAYS

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Online publication date: 14 August 2002

To cite this Article Kou, M. R. Sun , Mendioroz, S. , Salerno, P. and Muoz, V.(2002) 'THE APPLICATION OF ELECTRON SPIN RESONANCE SPECTROSCOPY TO STUDIES ON COPPER(II) DOPED PILLARED CLAYS', Spectroscopy Letters, 35: 4, 565 — 580
To link to this Article: DOI: 10.1081/SL-120013891
URL: http://dx.doi.org/10.1081/SL-120013891

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SPECTROSCOPY LETTERS, 35(4), 565–580 (2002)

THE APPLICATION OF ELECTRON SPIN RESONANCE SPECTROSCOPY TO STUDIES ON COPPER(II) DOPED PILLARED CLAYS

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ABSTRACT

Pillared montmorillonites have been synthesized by treating Na-montmorillonite with Al_{13} or Zr_4-polymer solutions, prepared either by stirred or refluxed methods. The interaction of exchangeable copper(II) with these materials was studied by means of electron spin resonance (ESR) spectroscopy. These studies show that in general both mobile and immobile Cu(II) are present. Also, ESR measurements indicate the presence of a distorted octahedral cupric species in the micropore regions that is chemisorbed to an Al_{13} or Zr_4 pillar by displacement of some H_2O ligands. The nature of Cu(II) is dependent on the interlayer spacing, the dehydration state of the pillars and

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the method of preparation, especially of the Zr_4-polymer. At high temperature, copper structure changes from octahedral to square planar which strongly interacts with the dehydroxylated polymers. XPS helps to clarify the studied phenomena.

Key Words: Pillaring; Montmorillonite; Electron Spin Resonance (ESR); Copper

INTRODUCTION

Smectite clay minerals, such as montmorillonite, are provided with several textural and chemical properties, such as high surface area porosity, surface acidity and cation exchange capacity, that make them highly suitable for use as catalysts and catalyst supports.

In a previous paper,[1] we studied the catalytic activity of naturally occurring silicates as carriers for copper catalysts in methanol conversion to methyl formiate. We found that depending on the cations' location (either on the external or interlamellar surface), there were different types of interaction, including the oxidation state of cations, which affects the behaviour of the resulting catalyst.

In researching the effect of different environments on the activity of copper catalysts on methanol conversion, we have synthesized pillared clays by exchanging the interlayer cations of the same montmorillonite as that above, with bulky metal hydroxy polymeric inorganic cations, such as $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ and $[Zr_4(OH)_8(H_2O)_{16}]^{8+}$, which act as molecular props between the smectite layers, constituting well established porous systems, to which copper has been incorporated after calcination at 500°C. After copper incorporation, the behaviour of the resulting material is changed depending, among others, on 1) the copper location either on the external surface of the clay lamellae or into the confined space among pillars (with or without interchange with the remaining cations); 2) the making part of the pillar geometry, either through incorporation into any of the oligocation -OH constituents or even substitution of any of the corresponding Me- components; 3) the self formation of oligocations, which could compete with the main ones in pillaring the clay.

Electron Spin Resonance (ESR) Spectroscopy is a physical technique, that can yield a wide range of detailed information relating to: a) the mobility of hydrated ions in the interlamellar space of the clay expanding lattice, using transition metal ions or organic radical cations as "spin probes". b) the distribution of lattice charge in clays. c) the reactions of

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adsorbed molecules on the external and interlamellar surfaces involving the formation and stabilization of free radicals. d) the nature of the interlamellar water-cation layers in hydrated smectites and vermiculites. e) the study of cation orientation in restricted water layers on phyllosilicate (smectite) surface.[2–9] These studies are based on the fact that when paramagnetic exchange cations are present in these clays, their ESR spectra serve as sensitive probes of both structural and dynamic properties of the ions' local environment. Taking into consideration the paramagnetic characteristic of the Cu(II) ion, the purpose of the present work has been to investigate, using ESR, the structure and location of the doped Cu(II) ions in the interlayer region of a Spanish montmorillonite containing hydroxy aluminum or zirconium pillars.

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EXPERIMENTAL

Sample Preparation

The starting material was a montmorillonite, having the chemical formula $(Si^{4+}_{7.74}Al^{3+}_{0.26})_T(Al^{3+}_{2.5}Mg^{2+}_{1.30}Fe^{3+}_{0.25}Ni^{2+}_{0.003})_OO_{20}(OH)_4(Ca^{2+}_{0.21}Na^{+}_{0.85}K^{+}_{0.11})_{CC}$ and $CEC = 61.6\,meq/100\,g$, $S_{BET} = 87\,m^2/g$, $V_p = 0.121\,cc/g$, $d_{001} = 13.27\,Å$, from la Serrata de Nijar, Almería, SE of Spain. It was provided by Minas de Gador S.A. In order to prepare the pillared materials, the $\leq 2\,\mu m$ size fraction of previously obtained Na-Montmorillonite ($S_{BET} = 77\,m^2/g$, $V_p = 0.093$ cc/g, $d_{001} = 12.1\,Å$ was used.

Pillared clays were prepared using the cross-linking method,[10,11] by which the oligomer is made separately and then incorporated into the clay particles. In the study, two different pillaring agents $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ and $[Zr_4(OH)_8(H_2O)_{16}]^{8+}$ were used:

Hydroxy aluminium solutions were prepared by the slow dropwise addition of a 0.5 M NaOH solution to a 0.2 M solution of $AlCl_3{\cdot}6H_2O$. Two OH/Al molar with a ratio of 1.8, 1.6 and an Al/clay ratio of 20 meq/g clay have been used. The pillaring solutions were aged for 2 h at 60°C prior to clay incorporation.

Hydroxy zirconium cations were prepared from the hydrolysis of $ZrOCl_2{\cdot}8H_2O$ (0.1 M) aged under two different conditions: a) Stirring (SR): 1 h, 25°C, b) Refluxing (R): 24 h, 100°C. After 24 h of equilibration, the clay suspensions were dialyzed against distilled water (1 litre/g of clay), renewing the water every day until chloride free (an electric conductivity of around 20 μs/cm). Further details on the pillaring can be found elsewhere.[12,13] Samples will be identified from now on as MeP/x/y, where Me is for Al or Zr respectively, x for the OH/Al relation in the case of AlPILCs and for

the meqZr/clay relation in the case of ZrPILCs and y for SR (stirring) or R(reflux).

The pillared clays oven dried at 60°C and calcined at 500°C were doped by exchange with Cu(II) as to have a concentration around 1%, by stirring 1 g of sample with 1.5 cc of 1 M $Cu(NO_3)_2$ in 25 cc distilled water for 12 h at room temperature. The clays were washed twice with distilled water at room temperature and once more with 25 cm^3 of hot distilled water, filtered and oven-dried at 100°C. Cu-doped samples will be referred as CuMeP/x/y.

MATERIALS AND METHODS

X-ray diffraction (XRD) was carried out on a Siemens Diffractometer model Kristalloflex D-500 using Ni-filtered CuKα radiation and a 2θ scanning speed of 2°/min. Nitrogen adsorption isotherms at 77 K were determined with a Micromeritics ASAP 2000 sorptometer on samples outgassed at 200°C for 16 h. Cu(II) was analyzed by AAS in a Perkin Elmer 3030 Spectrofotometer.

XPS spectra were recorded in a Leybold-Heraeus LHS10 equipment. Unmonochromatized Mg Kα X-ray radiation ($h\nu = 1253.6$ eV) operated at 10 mA and 12 kV was used as exciting source. For spectra acquiring, powdered samples pressed under vacuum at 250–500 kg/cm^2 in a cylindrical holder (9 mm diameter, 1 mm height) were introduced in the analysis chamber where a residual pressure of 6E-9 Torr (1 Torr = 133.3 N m^{-2}) prior to analysis was maintained. The spectrometer was equipped with a high-pressure cell to carry out treatments at high temperatures. Always the C 1 s line at binding energy of 284.5 eV was used as internal standard. The intensity of various XPS peaks was determined using S-shaped background subtraction and integration of peaks areas. The atomic ratios were estimated from the integrated intensities of Si 2p, Al 2p, Zr $3d_{3/2}$ and Cu $2p_{3/2}$ peaks using the Wagner et al. sensitivity factors.

The spectra ESR were recorded as first derivatives with a Bruker ER 200D Spectrometer operating in X-band ($\nu = 9$–10 GHz) with 0.1–100 mW power. The spectra were recorded at 77 K, and a DPPH standard ($g = 2.0036$) was used to calibrate the magnetic field. The spectrometer is connected to a Bruker Data Station model ESP 1600 which enables data treatment and accumulation. Samples of around 30 mg were placed in a quartz cell with greaseless stopcocks and outgassed by flowing nitrogen at 77 K during 1 h, and work pressure $\approx 10^{-4}$ Torr. Furthermore, the samples were heated at different temperatures during 1 h, frozen at 77 K and finally the spectra were taken.

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RESULTS AND DISCUSSION

Table 1 shows the most relevant physico-chemical characteristics of the Al or Zr pillared clays after calcination at 500°C. Diffractograms corresponding to some of ZrPs, especially 20SR and 20 R samples, do not offer the increase in basal spacing expected from pillaring or even that corresponding to the starting clay, indicating that delamination instead of pillaring has occurred under the conditions used. No changes in the diffractograms resulted from the incorporation of Cu(II).

With respect to texture, the addition of Cu reduces the surface area in AlPs whereas it does not affect that in ZrP, except in ZrP/20/SR which experiences a 26% increase. In all samples, Cu (II) incorporation was slightly less than proposed (being lower in ZrPs than in AlPs). In Table 1, the main physico-chemical characteristics of the samples before and after Cu-addition are shown.

Figure 1 shows the ESR spectra recorded at 77 K of sample AlP/20/1.8 after degassing in vacuum at 100, 150 and 200°C, Figs. 1a, 1b and 1c, respectively. All three spectra show similar ESR parameters with $g = 2.37–2.36$, $A = 154–145 \times 10^{-4}$ cm^{-1}, $g_{\perp} = 2.07–2.06$.

In the samples heated at 100° and 150°C, the spectra are less intense and better resolved than after 200°C heating. The spectra are highly anisotropic and show a motionally restricted Cu(II) ion, as if it were chemisorbed on some surface site. The observed ESR parameters are similar to those reported by Kukkadapu and Kevan[14,15] for A_{chem}, from which it can

Table 1. Main Physico-chemical Properties of Cu-Doped Pillared Clays

Sample	Cu (%)	Me(%)	S_{BET} (m^2 g^{-1})	d_{001} (Å)*
AlP/20/1.8	–		158	16.3
AlP/20/1.6	–		184	16.02
CuAlP/20/1.8	0.8		101	15
CuAlP/20/1.6	0.9		150	16
ZrP/20/SR	–	9.63	149	–
ZrP/20/R	–	9.58	221	–
ZrP/2/SR	–	4.69	78	13
ZrP/2/R	–	4.50	158	12
CuZrP/20/SR	0.6		189	–
CuZrP/20/R	0.7		222	–
CuZrP/2/SR	0.4		92	13
CuZrP/2/R	0.5		161	12

*After 500°C calcination.

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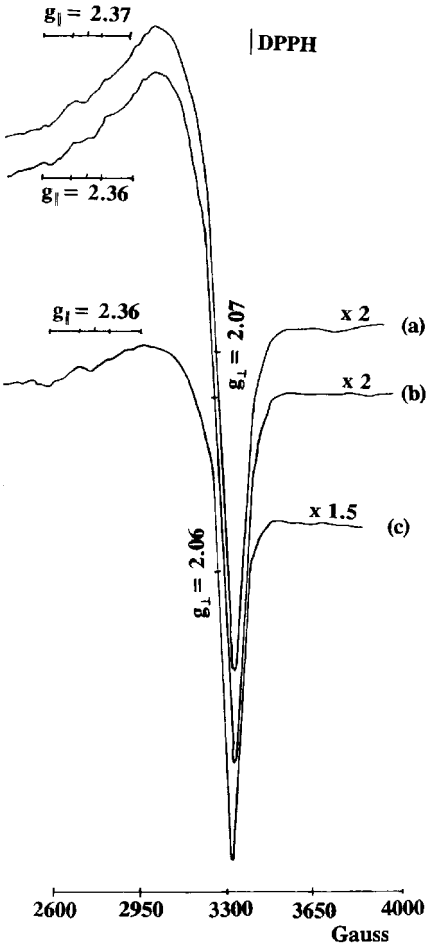

Figure 1. ESR spectra at 77 K of A1PILC/20/1.8, 1 h evacuated at: a) 100°C, b) 150°C, c) 200°C.

be deduced that at first and up to 150°C temperature, copper is as hydrated Cu(II), with an octahedral structure and with one or more ligands interacting with the aluminum pillar through the AlOH and/or the $AlOH_2$ groups of the keggin cation to likely form $[Al(OHOH_2)_XCu(H_2O)_{6-x}{}^{2+}]$. The bond is of the irreversible chemisorption type, and of the same type that on noncrystalline alumina, gibbsite, bohemite and even OH-montmorillonite[6].

A decrease in the Cu(II) signal intensity and a slight change in the ESR parameter is apparent with temperature increase. Thus, after 150°C

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treatment the spectrum is slightly broader indicating a closer association of Cu(II) with the pillar, likely coming from partial dehydration of the pillar surface, resulting in a higher availability of -AlOH groups for coordination and giving rise to a new species, with square-planar symmetry assigned to -$Al(OHOH_2)_xCu(H_2O)_{4-x}^{2+}$.

A broad Fe^{3+} signal near $g = 4$ was observed in the pillared samples, as well as in the original clay (Na-Mont), Fig. 2. This Fe^{3+} signal is composed in the Na-Mont of two resonances: the lower field Fe^{3+} line at $g = 4.19$ attributed to Fe^{3+} adjacent to Al^{3+} in the octahedral sheet of the layer, and the high field Fe^{3+} line at $g = 3.65$, corresponding to Fe^{3+} adjacent to a negative charge site.[14] The latter disappears with the incorporation of

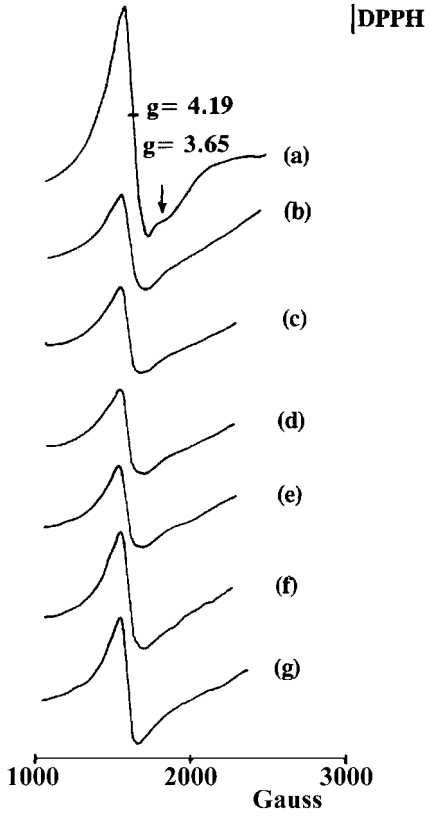

Figure 2. ESR spectra at 77 K of Fe^{3+} near $g = 4.19$ of: a) NaMont, b) A1PILC/20/1.8 evacuated at 70°C, c) 100°C, d) 150°C, e) 200°C, f) 250°C, g) 300°C.

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Al oligocations into the clay indicating that a complete interchange and neutralization of the interlayer residual negative charge was effected. No additional change with the temperature is apparent after Cu(II) incorporation into the samples.

The spectra corresponding to sample ZrP/20/SR, outgassed during an hour at 70, 100 and 150°C and recorded at 77 K are shown in Figs. 3a, 3b and 3c, respectively. Spectrum 3a shows an anisotropic Cu(II) species with $g = 2.34$, $A = 132 \times 10^{-4}\,cm^{-1}$ and $g_{\perp} = 2.06$, which is similar to the B species reported by Kukkadapu et al.[16] and corresponds to a square planar cupric ion at the center of the oxygen plane in a polymeric Zr_4 coordinated to hydroxyl groups. It must be realized however, that since this sample is delaminated and not pillared (Table 1), species B is not incorporated to a

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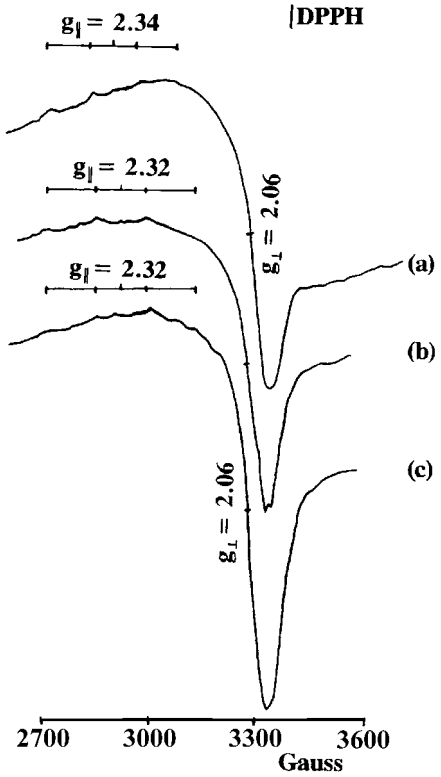

Figure 3. ESR spectra at 77 K of ZrPILC20SR evacuated at: a) 70°C, b) 100°C, c) 150°C.

pillar, as Kukkadapu et al. reported, but only to a Zr_4 polymer whichever its position in the sample. At higher treatment temperature, 100°C, the g value is slightly lower ($g = 2.312$) and A is slightly higher ($A = 154 \times 10^{-4}$ cm^{-1}) than above, indicating the strengthening of the equatorial bond along the x and y axes. The weak intensity of the peak suggests the presence of a partially dehydrated phase of hydroxy-zirconium, with changes in the Cu cation surroundings. On evacuating at 150°C, the resulting species is identical to that at 100°C, a broadening of the signal makes the dehydration process more apparent. The Cu species is then similar to the B species in a Zr_4-polymer but now coordinated to oxygens (species E). ESR parameters are most characteristic of a distorted square-planar symmetry and suggest that the Cu(II) complex is bound to Zr_4 polymer (pillaring or not) at the same coordination position, but with two different hydration states (species B and E).

On comparing the spectra corresponding to SR samples with 2 and 20 meq/g clay acquired at 77 K under 10^{-4} Torr and 100°C evacuation, Figs. 4a and 4b respectively, no difference in the ESR parameters is shown in spite of the different structures of the clays, pillared and delaminated respectively as said before, except for a slightly higher g value (2.323) in Zr2SR corresponding to species E as well. A basal spacing of 13 Å as in sample 2SR, is not compatible with the dimensions of a $[Zr_4(OH)_{14}(H_2O)_{10}]^{2+}$ cation ($10 \times 10 \times 4.6$ Å), not even if the Zr_4 lies parallel to the layers forming a monolayer between them. Then, it must be assumed that the Zr_4 cation not only lies parallel to the clay lamellae, but also that it must be completely dehydroxylated, although preserving its structure in order to fulfill the XRD requirements, and Cu(II) is incorporated to the oligocation at the center of the oxygen plane. Thus, the slight differences in g value must be due to the different surroundings of the Zr_4 cation, inter or extralayered located in the clay. Incidently, it must also be concluded that the 500°C treatment applied to the Zr-interchanged clays to form pillars is too much drastic and a complete dehydroxylation of the Zr_4 cation occurs decreasing the expected pillar dimensions.

On ZrP/2/SR the signal corresponding to Fe^{3+} shows the high field peak at $g = 3.65$ said above, ascribed to Fe^{3+} adjacent to a negative charge site, which denotes an incomplete nullification of the negative charge in the interlayer and hence an incomplete interchange. This signal disappears on sample ZrP/20/SR with 20 meq Zr/g clay in the synthesizing step.

Refluxing the pillaring Zr solutions results, as said above, in a high polymerization of Zr altogether with a quite low solution pH that causes a great disordering of the clay structure first through delamination and finally through solution of the clay's octahedral layer. The product, once doped with copper, also show important changes in the Cu ESR spectrum with

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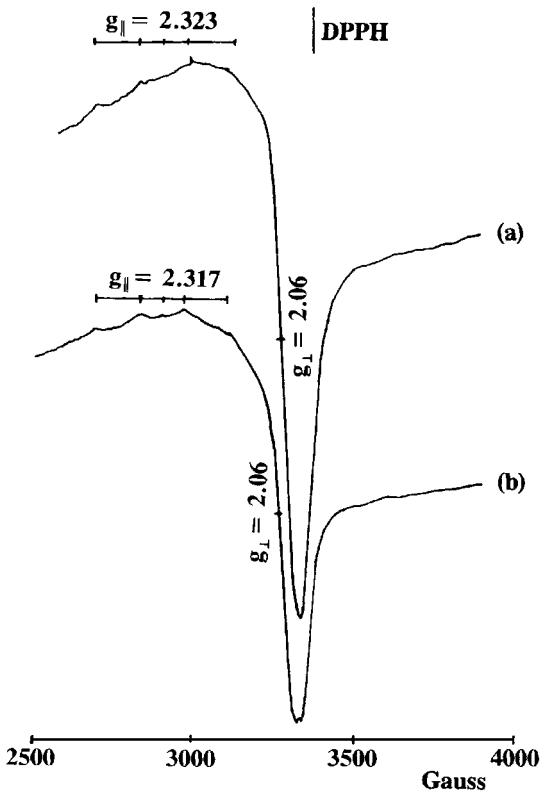

Figure 4. ESR spectra at 77 K of: a) ZrPILC2SR and b) ZrPILC20SR evacuated at 100°C.

respect to the stirred samples. Thus, sample ZrP/2/R shows an isotropic Cu^{2+} line with $g_{iso} = 2.17$, which reveals the presence of the A_{mobile} species identified by Kukkadapu and Kevan,[14,17] it is to say of a freely tumbling octahedral cupric ion ($Cu(H_2O)^{2+}_6$) species with no interaction with the substrate. This line is very similar to that observed for aqueous solutions containing $Cu(H_2O)_6^{2+}$ ions which undergo tumbling and/or Jahn-Teller distortions rapid enough as to mediate the anisotropy. Such a species has also been observed on unpillared smectite at 100% relative humidity,[15] Cu(II)-montmorillonite after adsorption of pyridine, glycine and β-alanine,[2] and Cu(II)ion doped Ca(II) and Zn(II)-montmorillonite.[3]

Outgassing the sample at 100 and 150°C respectively, the isotropic species changes to an anisotropic one, with $g = 2.36$, $A = 122 \times 10^{-4}\,cm^{-1}$

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and $g_{\perp} = 2.07$. The anisotropic spectrum indicates a motionally restricted Cu(II) ion, in this case the octahedrally coordinated $Cu(H_2O)_6^{2+}$, at difference of the square-planar detected on the stirred sample, with one or more of its ligands interacting with the Zr_4 ion. This species in the refluxed sample is designated as B_1 to differentiate it from species B in the stirred sample.

Since, as above, the interlamellar distance in the sample is 12 Å (Table 1), it cannot accommodate the octahedral hydrated cupric ion ($Cu(H_2O)_6^{2+}$) and even less to allow for the free tumbling of the cation, then, it must be accepted that Cu(II) must be located on the external surface of the clay without any bond to the Zr_4 polymer at low temperature. The low density of Zr_4 in this sample (Zr/clay = 2 meq/g), helps to preserve the isolated $Cu(H_2O)_6^{2+}$ characteristics. An increase in the treatment temperature may cause mobility of the cations that finally result in their chemisorption on the Zr_4 cation. The contrasting behavior between B_1 and B may be due to the formation of different Zr_4-polymeric species under stirred and refluxed conditions. The ratio of the immobile/mobile component increases with the temperature. Since the immobile component of Cu in AlPILCs, has been ascribed to Cu(II) bound to an Al-OH group of Aluminum hydroxides in the Al_{13} pillar, then, the immobile component observed here may be due to Cu(II) bound to the external shell of the zirconium pillars.

Figure 5 shows the ESR spectra at 77 K of ZrP/20/R evacuated at: a) 70°C, b) 100°C, c) 150°C, d) 200°C, e) 250°C, f) 300°C. No clear hyperfine structure is observed in the spectra of ZrP/20/R after treatment in the 70–300°C range (Fig. 6), except for a slight signal at g = 2.016 probably due to overlap of the hyperfine components or to a center whose nature and relation with the crystallinity and chemical composition of the sample is not clear. In any case this signal disappears with the temperature. Probably, the position of Cu^{2+} in sites where the spin-net relaxation time is very short may be adduced to explain why there are not observable signals in the ESR spectra. Here, the lack of the low field signal in the Fe^{3+} ESR (g = 3.65), seems to indicate that interchange has been complete.

In order to have a deeper insight of the samples, they were examined through photoelectron spectroscopy, taking as internal standard the BE corresponding to C1s at 284.5 eV as said above. The obtained results are given in Table 2.

On Cu/AlPILC1.8 the $Cu2p_{3/2}$ line shows two copper states with binding energies of 936 and 933.8 eV which corresponds to Cu(II) and Cu(I) respectively, later confirmed through the secondary peak corresponding to the Cu2p line. The presence of a partially reduced Cu(I) can be understood as if the interaction of Cu(II), present in the precursor salt, with the Al_{13} cation was not strong enough as to stabilize it, leading to reduction to Cu(I)

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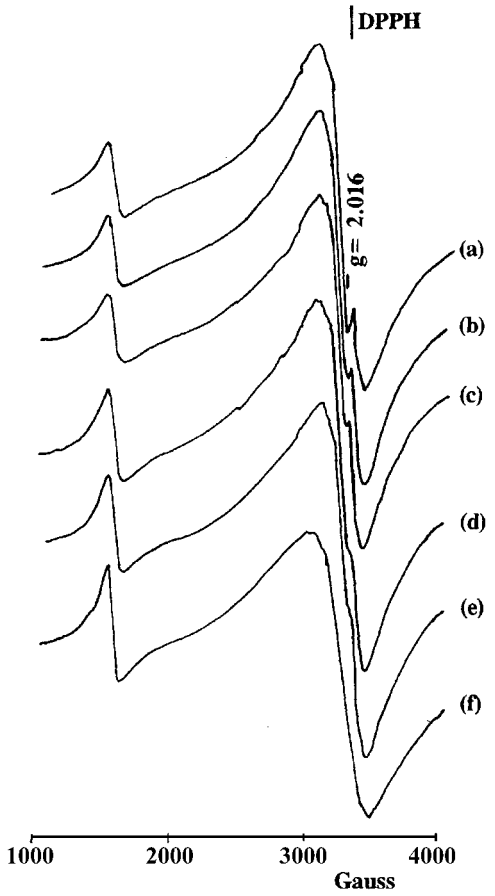

Figure 5. ESR spectra at 77 K of ZrPILC20R evacuated at: a) 70°C, b) 100°C, c) 150°C, d) 200°C, e) 250°C, f) 300°C.

under the electrons beam of the technique. With respect to ZrPILCs, the same two Cu states are visible, one, more oxidized at ~ 935 eV and the other at ~ 933 eV. The extent of the reduced fraction denotes, at least qualitatively, that the interaction with the Zr_4 substrate is smaller in SR than in R samples and hence, it helps to conclude that a different Zr species has been generated in the $ZrOCl_2$ hydrolyzing step. Comparing the atomic Zr/Si relations obtained from elemental analysis and XPS, it is visible that the amount of Si on the surface against that in the bulk is higher in ZrP20R

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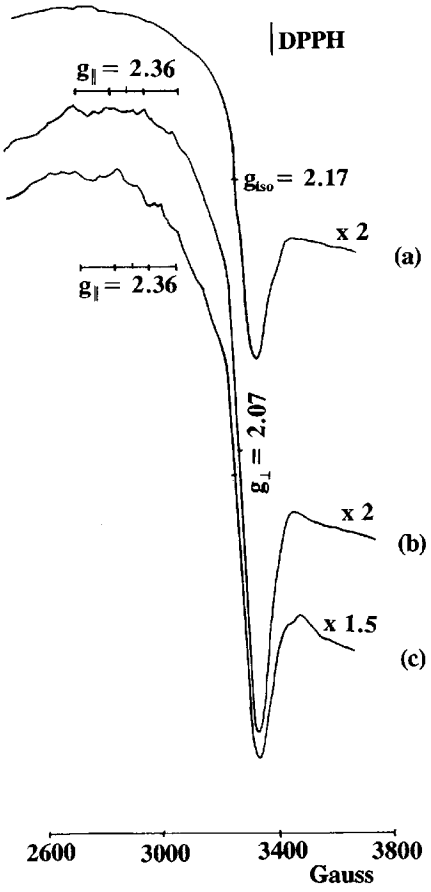

Figure 6. ESR spectra at 77 K of ZrPILC2R evacuated at: a) 70°C, b) 100°C, c) 150°C.

than in 20SR sample, with the same Zr content, whereas it is of the same order in samples 2 R and 2SR. That means that different $ZrOCl_2$ hydrolysis conditions result not only in a different Zr species but also in a modification of the parent material surface, through partial solution of the clay, the lower the pH the more, and further silica deposition on the clay surface. Cu/Zr ratio is similar in all samples (slightly higher on CuZrP2SR) independently of the Zr amount at the surface, confirming the incorporation of Cu to the Zr_4 polymer and hence related to the amount of Zr present in the sample.

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Table 2. Binding Energies (eV) and Surface Atomic Ratios

	Binding Energies (eV)				Atomic Ratio	
Sample	Si2p	Al2p	$Zr3d_{3/2}$	$Cu2_{3/2}$	Zr/Si	Cu/Zr
Cu/AlPILC1.8	103.2	74.8	—	933.8 (84%) 936.0 (16%)	—	—
Cu/ZrPILC20SR	102.8	74.7	182.6	933.4 (87%) 935.5 (13%)	0.333 0.166	72E-4
Cu/ZrPILC20R	102.8	74.7	182.7	933.5 (74%) 935.7 (26%)	0.106 0.194	66E-4
Cu/ZrPILC2SR	103.0	74.8	182.9	934.0 (91%) 935.9 (9%)		94E-4
Cu/ZrPILC2R	102.8	74.7	182.7	933.5 (87%) 934.1 (13%)		67E-4

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As a conclusion of this work, it can be said first that both, octahedral and square planar structures of Cu(II) have been observed in samples of montmorillonite with aluminum/zirconium hydroxy pillars (at 70°C). The octahedral cation is present mainly in AlPILC where it is attached to an Al_{13} forming pillars in the micropore region by displacement of some H_2O ligands, but also in ZrPILCs when the Zr concentration is low and the refluxing method has been used in the synthesis; here, it is freely moving on the external surface of the clay, near to a Zr_4 cation. This octahedral species changes under thermal treatment to a square planar structure bound to the external shell of Al_{13} or Zr_4 polymers. In the remaining cases, it is to say, when higher concentrations of Zr and/or stirring is used as a method of synthesis, Cu(II) adopt a square-planar structure occupying the center of the oxygen plane in a completely deshydroxylated Zr_4-polymers with or without pillar formation inside the montmorillonite structure. Those species retain their individuality at least until a 300°C calcination, although they increase their interaction with the support as the temperature rises.

The method of hydrolyzing the starting $ZrOCl_2$ and the pH reached in the hydrolysis gives rise to the different Cu^{2+} species present in the samples at ambient temperature, as a consequence of the different Zr_4 polymers formed, and the changes supported by the clay in the step of incorporation of the oligomer.

Besides, it can be concluded that only high metal/clay ratios result in total cation interchange, a more drastic condition being necessary with low metal/clay ratio to provide the same effect.

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Received June 14, 2001
Accepted May 1, 2002

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