

CHARACTERIZATION OF SEVERAL NATURAL LATERITES BY USING X - RAY PHOTOEMISSION SPECTROSCOPY (XPS)

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Abstract

A surface analysis of several samples of Venezuelan laterites is reported. This analysis is done mainly with XPS, though Thermogravimetry (TGA) and Differential Thermal Analysis (DTA) have also been employed. Two oxygen species have been detected, one of them in the form of $O^=$ in the oxides Fe_2O_3 , Al_2O_3 and SiO_2 , the other as OH^- within the crystal structure of $FeOOH$, $AlOOH$ and $Al(OH)_3$. Our results show that the sample under study presents an incomplete phase change from goethite to hematite. Only Fe, Al, Si and O were detected in the surface of the samples. The surface stochiometry of the detected elements was determined.

Key words: laterites, Aluminum oxides, Iron oxides, gibbsite, goethite.

INTRODUCTION

Laterites are residual products derived from a wide variety of rocks by intensive chemical weathering under strongly oxidizing and leaching conditions. The chemical constituents can be present in the laterites under different crystallographic forms. Iron can be found as hematite (Fe_2O_3) and/or goethite α - $FeOOH$. Aluminum can be found as gibbsite (α - $Al(OH)_3$) [1,2] and/or bohemite (γ - $AlOOH$) and diasporé (α - $AlOOH$). Silicon can be present whether in colloidal form, or in quartz, which is the most common crystallographic form.

Several researchers [3,4,5,6] have studied the use of laterites as hydrocracking and HDM catalyst with excellent results.

METHODS

In the present work, thermogravimetric analysis (TGA), thermal differential analysis (DTA) and x-ray photoelectron spectroscopy (XPS) have been employed to study several samples of laterites. The samples were ground

and sieved in order to obtain a particle size of less than 150 microns. Each was analyzed in the natural state (NS) using XPS and TGA and also after calcination up to 550°C under air (AC). The thermogravimetric measurements were performed in a Sartorius microbalance with a mixture Oxygen-Helium as gas vector. The XPS measurements were taken with an A.E.I. ES200 B spectrometer at University of Lille I, France. Non-monochromatic $Al K\alpha$ radiation was used as x-ray source. Vacuum in the spectrometer was always better than 10^{-7} Torr.

RESULTS AND DISCUSSION

We have concluded that for all the LV samples the binding energy of the C_{1s} level (285.0 eV) from adventitious carbon, is a good reference. The surface stochiometry obtained from the XPS results is reported in table I for the LV samples in their natural state and after calcination. One must note that the O concentration presented correspond to the total Oxygen specie analyzed. The aluminum Al_{2p} , and Silicon Si_{2s} peaks do not shift in energy within the experimental error of about ± 0.2 eV. On the other hand, a shift toward

lower binding energies is observed for the Fe_{2p} peak after calcination. This Shift varies from 0.6 to 1.3 eV, except for the LV4 sample for which no shift is observed. This shift can be explained, as reported by studies of McIntyre [7], by assuming a deshydroxylation process of FeOOH (Fe_{2p3/2}: 711.0 eV); the iron oxidation state remains equal to +3 [7,8]. In the LV4 sample we obtain a binding energy of $771. \pm 0.2$ eV, which corresponds to the Fe_{2p3/2} level in Fe₂O₃ like species according to McIntyre [7]. For this sample we can assume that Fe is not hydroxylated in the natural state.

In figure 1 and 2 the O_{1s} peaks are shown. For natural samples, the O_{1s} peak maximum is situated around 533 ± 0.5 eV, except for the LV4 sample, for which the O_{1s} peak is located at about 532 eV. After calcination a large evolution of profile of the O_{1s} peaks can be observed, two maxims appear at about 533 and 530 eV. Again the LV4 sample behaves differently, since there is only one maximum at 531.2 eV. All the O_{1s} peaks exhibit wide profiles indicating the presence of several oxygen species. The component at 530.0 ± 0.5 eV may be assigned to oxygen either in H₂O or SiO₂. So, the decrease of this component calcination is associated to the loss of water. The remaining component is the assigned to oxygen in SiO₂ like species, and its strength can also be related to the amount of Si present in the respective samples. The component situated at 530 eV is related to oxygen in iron oxides like species and agrees with O²⁻ ions of the network [9,10]. The increasing intensity of the component on the calcinated samples is due to less water of OH⁻ groups bounded to Fe and its relative intensity can be related to the amount of Fe. The position of the intermediate component (531.2 and 532 eV range) is related to oxygen bounded to Al, and one must note that the energy positions of hydroxyl group and oxygen bounded to Al are very close [7,9-13]. So, it is rather difficult, at this stage, to specify the energy positions and relative intensities of this species in the laterites. Nevertheless, starting from the particular LV4 sample (without Si) a structural transformation from gibbsite (Al(OH)₃; O1s = 531.6 eV) is expected as we observe a shift in the O_{1s} spectra.

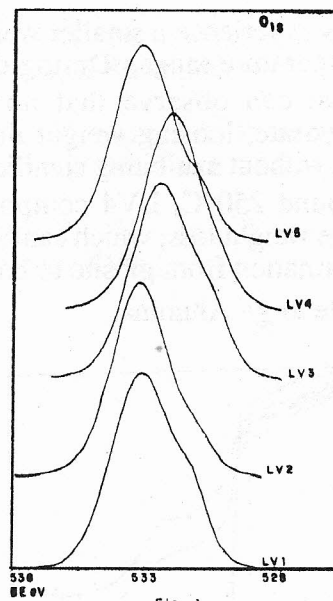


Fig. 1
The O_{1s} peak for the natural (NS) LV samples

Fig.1. The O_{1s} peak for the natural (NS) LV samples.

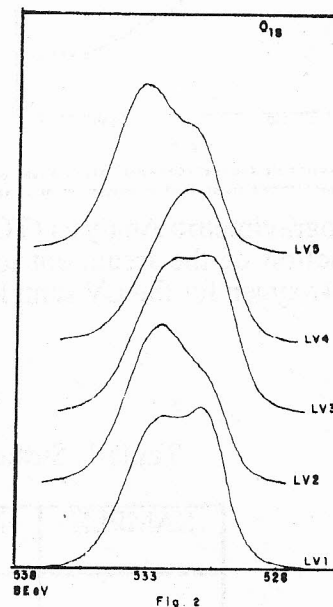


Fig. 2
The O_{1s} peak for the calcined (AC) LV samples

Fig.2. The O_{1s} peak for the calcined (AC) LV samples.

The weight loss as a function of the temperature (T) for different Venezuelan laterite samples are shown in figure 3. LV4 sample exhibits the highest weight loss of about 27% in the temperature range from 200°C to 600°C. The

other samples experience a smaller weight loss on the same temperature range. During this thermal treatment, we can observe that up to 200°C laterites dehydrate, losing weight due to water absorbed and without exhibiting significant change. Around 250°C, LV4 compound shows an appreciable weight loss, which can be attributed to the transformation from gibbsite to bohemite and from bohemite to χ -Alumina.

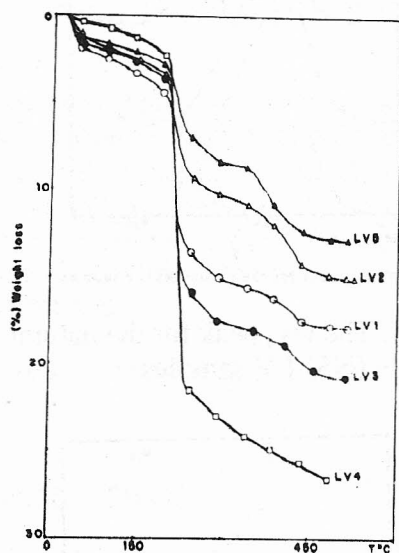


Fig. 3. Thermogravimetric Analysis (TGA) weight loss as a function of the treatment temperature under helium+oxygen for the LV samples.

Fig.3. Thermogravimetric Analysis (TGA) weight loss as a function of the treatment temperature under helium+oxygen for the LV samples.

Between 400°C and 500°C, an additional weight loss is observed which can be due to the complete transformation from bohemite to χ -Alumina [14]. The DTA results obtained on the laterite samples show two endothermic peaks that are observed at 250°C and 450°C attributed to the phase transformation from gibbsite to bohemite and from bohemite to χ -Alumina respectively, these results are in good agreement with TGA data.

CONCLUSION

The XPS results allow to determine the surface composition of natural laterites and the structural they undergo during thermal treatment. It is found that after the thermal treatment of the laterites the Si/Al ratio remains unchanged, the Fe/Al ratio exhibits a slight increase, and the O/Al ratio shows a large decrease loss of water and deshydroxylation. The structural transformation (are put forward due to) the $Fe_{2p_{3/2}}$ shift (transformation from goethite to hematite [15]) and the increase of all photoelectronic lines width. The TGA and DTA results specify the range of temperature for which the transformations occur. Two endothermic phenomena appear at 250°C and 450°C respectively and are related to the weight loss observed in the TGA experiments. In this range of temperatures from gibbsite to bohemite and then to χ -Alumina take place [14].

Table 1. Surface stochiometric obtained from XPS results.

SAMPLE	NATURAL STATE (NS)	CALCINED STATE (AC)
LV1	$Fe_{0.52}Al_1Si_{0.51}O_{4.64}$	$Fe_{0.53}Al_1Si_{0.55}O_{3.91}$
LV2	$Fe_{0.30}Al_1Si_{0.80}O_{4.47}$	$Fe_{0.36}Al_1Si_{0.85}O_{4.02}$
LV3	$Fe_{0.41}Al_1Si_{0.48}O_{4.28}$	$Fe_{0.56}Al_1Si_{0.85}O_{3.74}$
LV4	$Fe_{0.11}Al_1Si_{0.02}O_{2.27}$	$Fe_{0.14}Al_1Si_{0.02}O_{2.08}$
LV5	$Fe_{0.45}Al_1Si_1O_{5.25}$	$Fe_{0.58}Al_1Si_{1.02}O_{4.88}$

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