

	Experiment title: INVESTIGACION ON THE OXIDATION STATE AND LOCAL ENVIRONMENT OF METAL CATIONS IN TRANSITION METAL MIXED OXIDES CATALYSTS	Experiment number: CH-1816
Beamline: BM26A	Date of experiment: from: 10/03/05 8.00 h to: 12/03/05 8.00 h	Date of report: 25 th August 2005 <i>Received at ESRF:</i>
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Report:

According to the project plan, we recorded the XANES spectra at the V K-edge of mixed transition metal oxides with catalytic activity in the gas phase selective oxidation of light alkanes, most specially the one with the chemical composition $Sb_{0.15}MoV_{0.20}O_x$ submitted to different treatments. In the previous session, we recorded the XANES spectra at the Sb L_1 edge of these samples in order to determine the oxidation state of Sb, an information which is not easy to get by any other spectroscopic technique. The aim of these measurements was to find out if the modification in the oxidation state of Sb with the catalyst treatment can be correlated with changes in the coordination environment of V.

Some of the treatment used for the sample preparation are: i) calcination under N_2 at 600 °C, ii) treatment under N_2 at 600 °C followed by calcination with air at 450 °C, iii) catalyst ii after its use in the catalytic test, iv) oxidized with air at 280 °C and then treated with N_2 at 600 °C. The analysis of the Sb L_1 XANES spectra recorded in the previous session show that, as a general trend, in the catalysts heated with N_2 Sb is as Sb^{3+} , while when it is treated under oxygen or air in any stage of the catalyst preparation, Sb is partially oxidized and a mixture of Sb^{3+} and Sb^{5+} appear. However, the changes in the V K-edge of the same

samples are not so evident and it is not easy to find a correlation between the evolution of the V and Sb coordination state in the samples. As an example, Figure 1a and 1b show the V K-edge XANES spectra of the sample treated with N₂ at 600 °C, and with air at 280 °C. While in the former Sb is as Sb³⁺, in the latter there is a mixture of Sb³⁺/Sb⁵⁺ (50:50, approximately). However, only small differences are observed in the V pre-edge region. The main spectral features of the spectra are consistent with both V⁴⁺ and V⁵⁺. However, the former appear to be more probable according to our results.

Besides this, we investigated the oxidation state of V in the fresh samples of chemical composition Sb_{0.15}MoV_{0.20}Nb_{0.15}O_x synthesized at different pH, as the performance of the final catalyst depends on the specific sample preparation. In these catalysts, with Sb is as Sb³⁺, the oxidation state of V is not clear. As an example, figure 2 shows the XANES spectra of two samples synthesized at pH=1,5 (Figure 2a) and pH=4,3 (Figure 2b). Both spectra are consistent with V⁴⁺ in a, and only subtle differences are observed among them.

The results obtained will be correlated with the catalytic performance of the materials investigated, which will allow the publication of at least two paper which are under preparation.

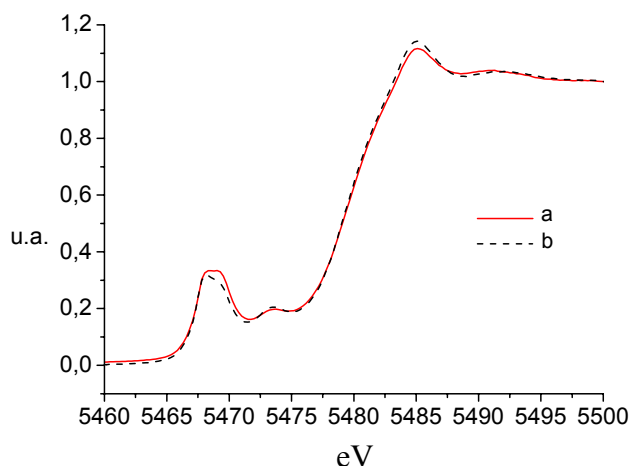


Figure 1

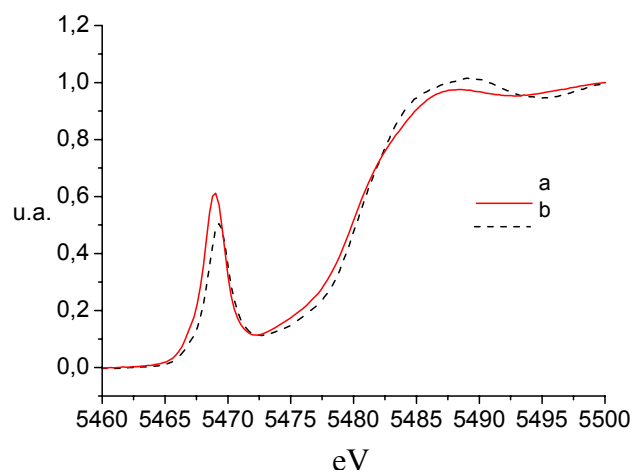


Figure 2