



**Experiment title: EXAFS and high resolution XANES study of the location, aggregation and oxidative state of iron species in Fe-silicalite, Fe-Al-silicalite and Fe exchanged ZSM-5 and Y zeolites**

**Experiment number: CH-695**

**Beamline:**  
BM8 GILDA

**Date of experiment:**  
from: 05/09/1999 to: 11/09/1999

**Date of report:**  
31/08/2001

**Shifts: 15**

**Local contact(s): Francesco D'Acapito**

*Received at ESRF:*

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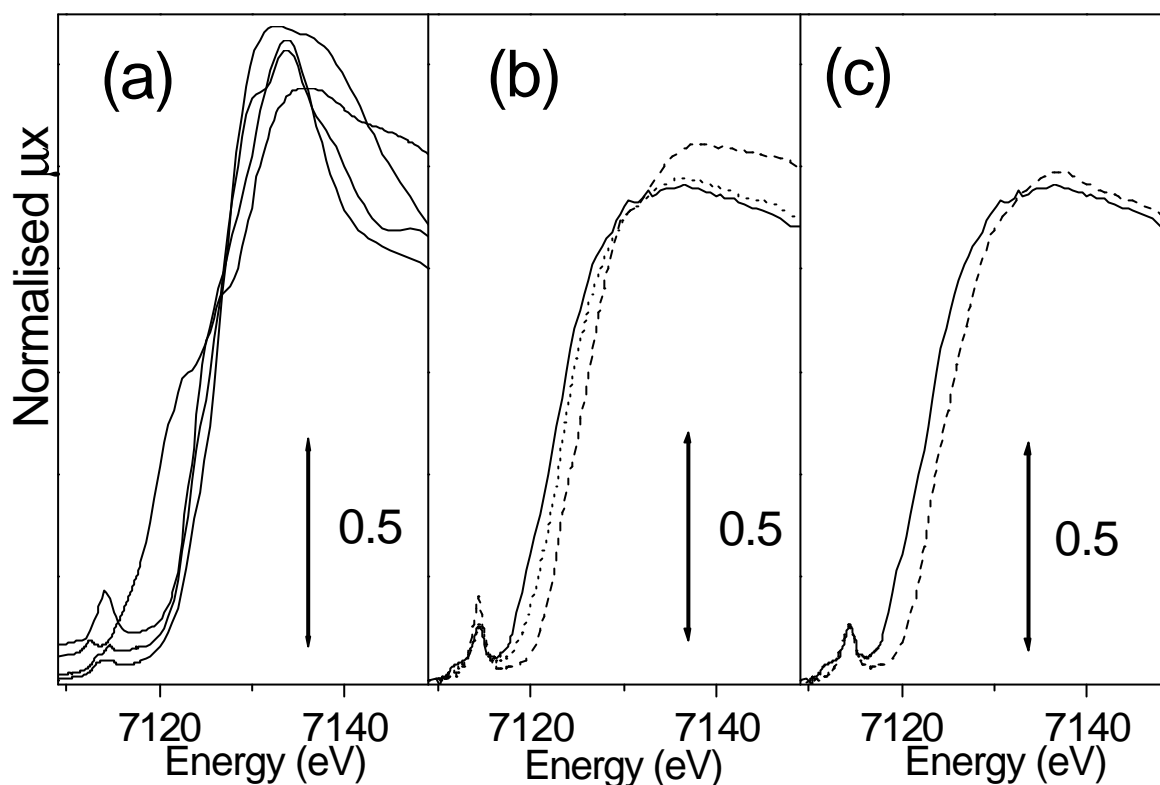
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### **Report:**

In previous works, reporting EXAFS/XANES data collected at LURE supported by IR, UV-Vis and EPR experiments, we have demonstrated that template removal at increasing temperature results in the progressive migration of Fe from framework into extraframework species [1-3].

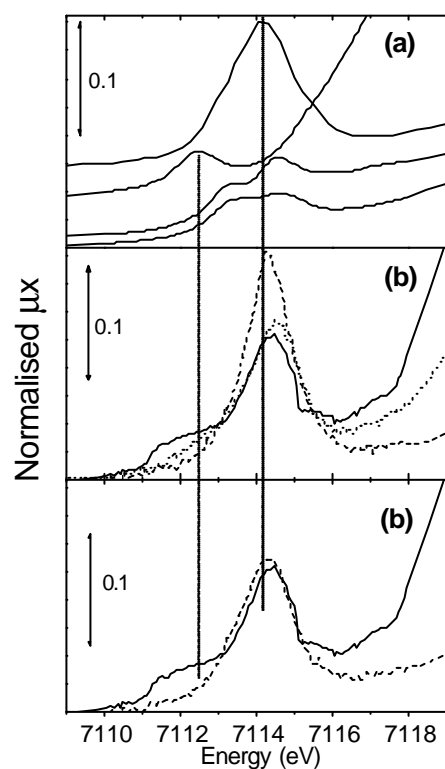
The present study was aimed to obtain a detailed, high resolution, XANES picture to determine both oxidation state and of local symmetry of Fe species upon template removal and interaction with N<sub>2</sub>O [4-6]. Among the measured model compound, we mention: FePO<sub>4</sub> (tetrahedral Fe<sup>3+</sup>); α-Fe<sub>2</sub>O<sub>3</sub>, (highly distorted octahedral Fe<sup>3+</sup>); and Fe(acac)<sub>3</sub> (quite perfect octahedral Fe<sup>3+</sup>); FeCp<sub>2</sub> (Fe<sup>2+</sup> in D<sub>5d</sub> symmetry). Edge position, white line intensity (Fig. 1a), pre-edge intensity and position (Fig. 2a) well reflects the oxidation state and the local symmetry of iron species in the model compounds. The A<sub>1</sub>→ T<sub>2</sub> pre-edge peak of Fe-silicalite with template (Fig. 2b) is even higher than that of FePO<sub>4</sub> (Fig.2a), indicating that Fe-silicalite with template is a better model than FePO<sub>4</sub> for Fe<sup>3+</sup> in T<sub>d</sub> symmetry. Fig. 1b and 2b also reports the effect of template burning, at increasing temperature on the XANES spectra. We note: (i) red shift of the edge (7123.6 → 7122.4 → 7120.6 eV); (ii) white line decrement (1.52 → 1.31 → 1.23); (iii) decrement (0.205 → 0.142 → 0.128) and broadening of the pre-edge peak; (iv) appearance of a new component at 7111.8 eV. Points (i) and (iv) highlight the reductive nature of the framework dislodgment process: migration to extraframework position is accompanied by Fe<sup>3+</sup> → Fe<sup>2+</sup> reduction; IR and EPR data support this important finding [4-6]. Point (ii) prove the high coordinative unsaturation of extraframework species as supported by the low Fe coordination number (EXAFS) and by the formation of Fe<sup>3+</sup>(NO)<sub>3</sub> adducts (IR). Point (iii) simply means that we lost the initial T<sub>d</sub> symmetry. Figs 1c and 2c prove that N<sub>2</sub>O is able to re-oxidize extraframework Fe<sup>2+</sup> species, as supported by IR and EPR [4-6].



**Figure 1** Part (a) XANES spectra of model compounds: from top to bottom  $\text{FePO}_4$ ,  $\text{FeCp}_2$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{Fe}(\text{acac})_3$  (Cp = cyclopentadienyl, acac = Acetylacetonate). The four spectra have been vertically shifted for clarity. Part (b) XANES spectra of Fe-Silicalite with template (dashed line), outgassed at 773 K and 973 K (dotted and full line respectively). Part (c) XANES spectra of Fe-silicalite outgassed at 973 K (full line, same curve as in part b, here reported again for direct comparison) and successively oxidised in  $\text{N}_2\text{O}$  at 523 K (dashed line).

#### References

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**Fig.2** As Fig.1: zoom .