



	<b>Experiment title: Structural and electronic characterization of Philips catalyst active site, in intermediate reaction step</b>	<b>Experiment number: CH-1435</b>
<b>Beamline:</b> BM8 GILDA	<b>Date of experiment:</b> from: 19/02/2003 to: 24/02/2003	<b>Date of report:</b> 27/02/2003
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## Report:

We write the present report only three days after the end of the experiment in order to prove to the *Review Committee* that the results expected in proposal CH-1435 have been achieved. Of course a more detailed report will follow in the next months once a proper EXAFS data analysis has been carried out.

The challenging

goal of proposal CH-1435 was the *in situ* collection of XANES and EXAFS data the  $\text{CrO}_x/\text{SiO}_2$  system, one of most efficient catalyst for ethylene polymerization [1]. The extremely high reactivity of the activated catalysts makes it highly sensitive to poisons (such as water, oxygen etc...) and really *in situ* conditions are therefore required. The use of an *ad hoc* conceived experimental cell [2] has allowed us to fulfill this request.

Figure 1 reports the XANES part of the x-ray absorption spectra of the  $\text{CrO}_x/\text{SiO}_2$  catalyst collected at high resolution (0.2 eV). The spectra have been collected during thermal activation in  $\text{O}_2$  and subsequent reduction in CO and ethylene respectively. The modification of the XANES features reflects the significant changes in the oxidation and coordination states of Cr. Thermal activation in  $\text{O}_2$  results in  $\text{Cr}^{6+}$  species characterized by a  $T_d$ -like coordination, as testified by the strong and sharp pre-edge peak at 5993.5 eV (1.9 eV FWHM). Interaction with CO results in a significant red-shift of the edge (8.0 eV), reflecting the reduction of chromium species to  $\text{Cr}^{2+}$ . Finally interaction with  $\text{C}_2\text{H}_4$  results in an increase of the ligand sphere around chromium sites, as testified by the significant increase of the white line intensity.

Even just from a superficial view of the  $k^2$ -weighted FT of the raw EXAFS data (Figure 2) the following aspects are evident: (i) the very short Cr-O distance observed on the oxidized sample reflect the presence of double bonds, which are broken by reduction with CO; (ii) the

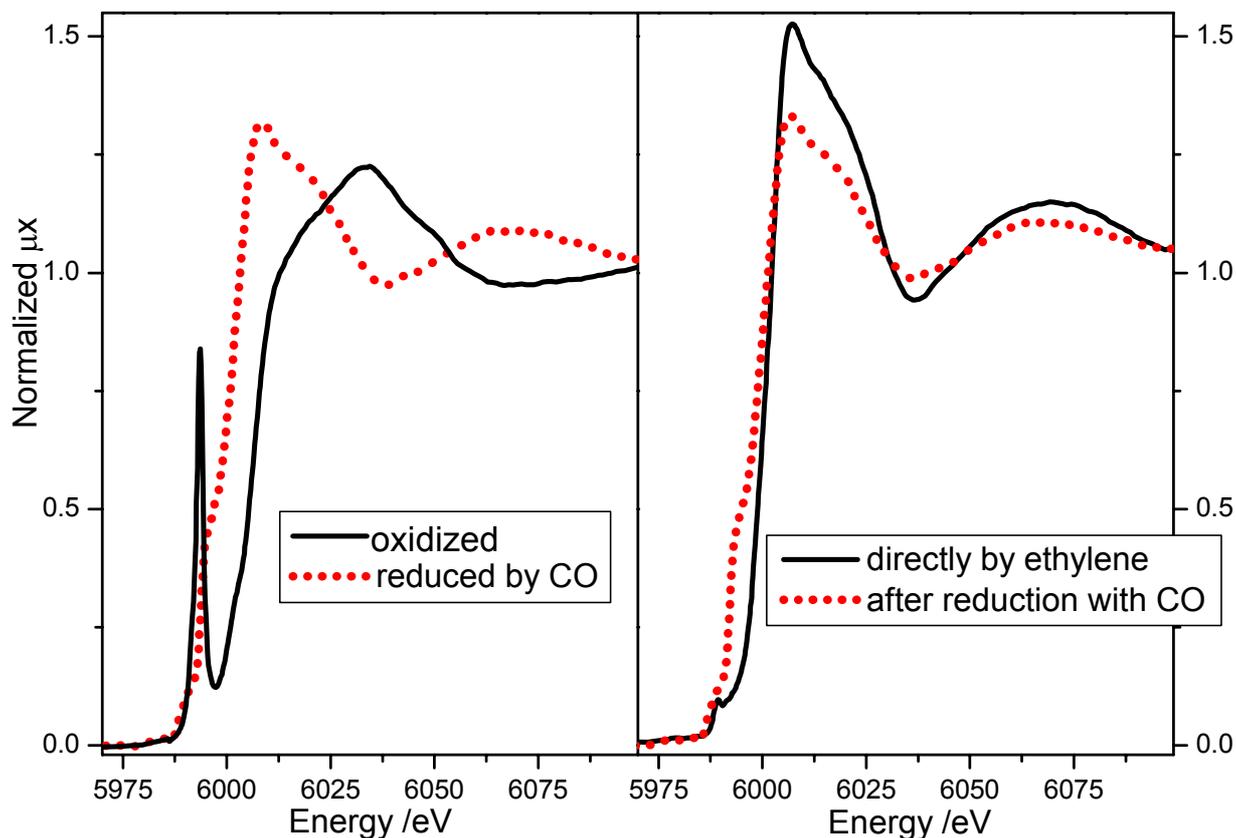


Fig. 1 High resolution XANES spectra of  $\text{CrO}_x/\text{SiO}_2$  catalyst after different *in situ* treatments.

chromium species present on the reduced catalysts exhibits a high coordinative unsaturation, testified by the low intensity of the corresponding first shell peak; (iii) the polymerization process allows Cr species to find new coordinative partners.

As a conclusion, we have been able to operate in real *in situ* conditions on such a delicate system, observing significant changes that are reasonable on the basis of the already established knowledge of the catalyst. We are confident that a careful XANES and EXAFS analysis will lead to a deeper understanding of the Phillips ethylene polymerization catalyst. Last but not least, preliminary tests, in reflexafs mode, with a single element detector, on Cr deposited on thin  $\text{SiO}_2$  films grown on Si(100) single crystals [3] have demonstrated that the S/N ratio is sufficient to collect good quality XANES/EXAFS spectra also on this model system.

## References

- [1] A. Zecchina, D. Scarano, S. Bordiga, G. Spoto, C. Lamberti, *Adv. Catal.*, **46** (2001) 265.
- [2] C. Lamberti, C. Prestipino, et al. *Nucl. Instr. Meth. B*, **200** (2003) 196.
- [3] J.W. Niemantsverdriet, P. Thüne et al. *J. Phys. Chem. B*, **101** (1997) (42) 8559; *J. Phys. Chem. B*, **105** (2001); 3073; *J. Catal.*, **183** (1999) 1.

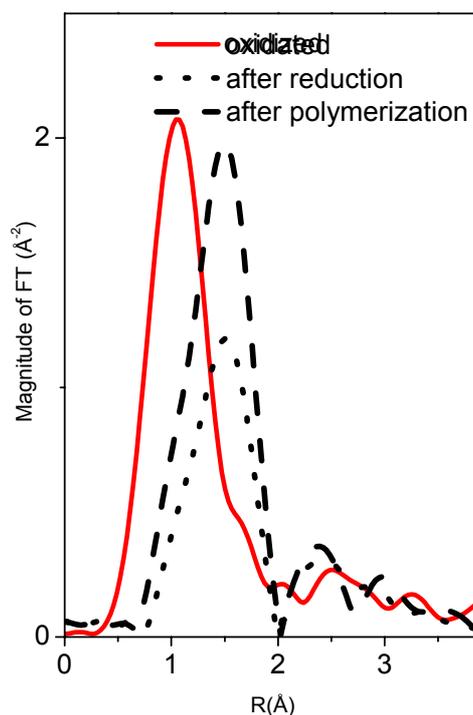


Fig. 2 FT of EXAFS data