ESRF	**Experiment title:** Electronic and spin state investigation of Cr species on SiO2: an attempt to understand the Phillips ethylene polymerization catalysts	**Experiment number**: CH-3107
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Report:

The aim of our work was to solve the electron and spin configuration of Cr in the Cr^{IV}/SiO_2 and Cr^{II}/SiO_2 that is fundamental to fully understand the mechanism of operation of the Phillips catalyst for ethylene polymerization [E. Groppo, C. Lamberti, S. Bordiga, G. Spoto and A. Zecchina, Chem. Rev., 105 (2005) 115-187]. The Cr sites in this catalyst is in fact currently highly debated in the literature showing the relevance of the topic. For these reason it is important to achieve a complete knowledge of the electronic structure of the Cr centers in Cr^{VI}/SiO_2, Cr^{IV}/SiO_2 and Cr^{II}/SiO_2 species in vacuo conditions in order to have a basis from where to start a study of a series of more complex systems. Our main interest focuses on the temperature dependence of Cr^{II}-$(CO)_n$ that will allow us to understand the changes in the Cr electronic structure needed to flip from non classical to classical carbonyls [D. Gianolio, E. Groppo, J. G. Vitillo, A. Damin, S. Bordiga, A. Zecchina, and C. Lamberti, *Chem. Commun*., **46** (2010) 976-978]. The same statements hold for the case of Cr^{II}/SiO_2/NO system. In particular an experiment performed on the Cr^{II}/SiO_2 and $Cr^{VI}/SiO2$ systems after ethylene polymerization can elucidate the electronic and spin structure of the Cr species interacting with the polymeric chain. For the measurements we started measuring Cr-based reference materials (as for instance Cr_2O_3). Two other classes of materials have been prepared and investigated: 1) $Cr_3(BTC)_2$ (or HKUST-1), a Cr based Metallorganic Material [C. Prestipino, L. Regli, J. G. Vitillo, F. Bonino, A. Damin, C. Lamberti, A. Zecchina, P. L. Solari, K. O. Kongshaug, and S. Bordiga, Chem. Mater., 18 (2006) 1337-1346] and 2) chromocene (CrCp2) hosted in porous polystyrene (PS) [J. Estephane, E. Groppo, J. G. Vitillo, A. Damin, C. Lamberti, S. Bordiga, A. Zecchina, *Phys. Chem. Chem. Phys.*, **11** (2009) 2218-2227], a system allowing to understand some aspect of the complex Union Carbide polymerization system (Cr/SiO2). After that we tried to measure our samples as done in the case of the proposal CH-2988 (see report).

The prepared samples were divided into three set. First set 1)Cr^{VI}/SiO_2 (in pellet @RT), 2)Cr^{VI}/SiO_2 (in pellet @LT 3) Cr^{VI}/SiO_2 + C_2H_4 (pellet) 4) Cr^{II}/SiO_2 (pellet) 5) Cr^{II}/SiO_2 + CO@RT (pellet) 6)Cr^{II}/SiO_2 + CO@LT (capillary) 7) Cr^{II}/SiO_2 + C_2H_4 (capillary) 8) Cr^{II}/SiO_2 + SiH_4 (capillary). Second set 9)$Cr_3(BTC)_2$ (as such capillary) 10)$Cr_3(BTC)_2$ (degassed capillary), 11)$Cr_3(BTC)_2$ + O_2(capillary), 12)$Cr_3(BTC)_2$ + NO(capillary). Third set 13) $CrCp_2$/toluene (capillary), 14) $CrCp_2$/PS (capillary), 15) $CrCp_2$/PS +CO @LT (capillary),16) $CrCp_2$/PS + NO 17) $CrCp_2$/PS +CH_3OH.

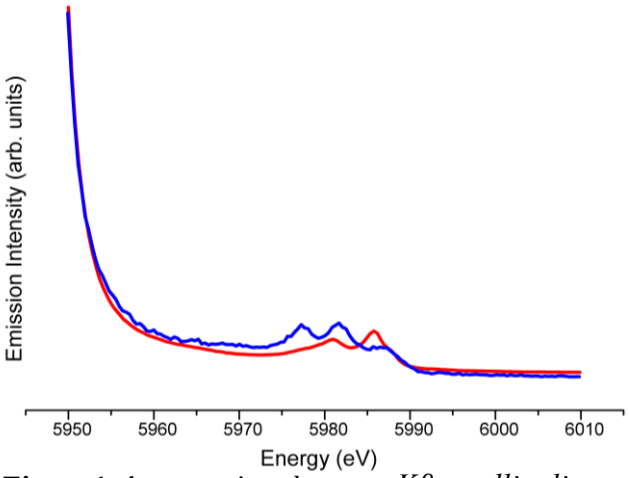

***Figure 1**. A comparison between Kβ satellite lines for systems 10) in red and 12) in blue.Note the modification after interaction with NO. The differents transitions involved in the process are identificated by means of density functional theory based code.*

Part 1. The sample from 1) to 7) that were the goal of the proposal showed very fast radiation damage: For example in the case of sample 3) the XANES showed already changes in the energy position and intensity of the white line after 2 seconds. In case of sample 1) we saw that radiation damage starts after 15 s under the beam. Interestingly, using the cryostat (available at ID26) did not change anything and the time after we saw radiation damage was exactly the same. For this reason it was only possible to collect XANES spectra but no XES and RXES maps. Regarding the XANES spectra we collect: for sample 1) and 2) 15 s XANES moving the pellet after each scan in order to increase the number of spectra and increase the statistics. For sample 3) and 4) we collect 1s XANES moving around the pellet while for 5), 6), 7) and 8) we moved long the capillary but it was possible to collect 20 s XANES per point. In order to adapt to this situation –**it had never happened before-** the ID26 staff developed a set of SPEC macros to allow, also in these very difficult cases, to collect complete RXES map. These macros have been tested during a night shift in an inhouse research (4 mA mode) in May 2010 and show the feasibility, in future, of this important project in order to collect the missed parts.

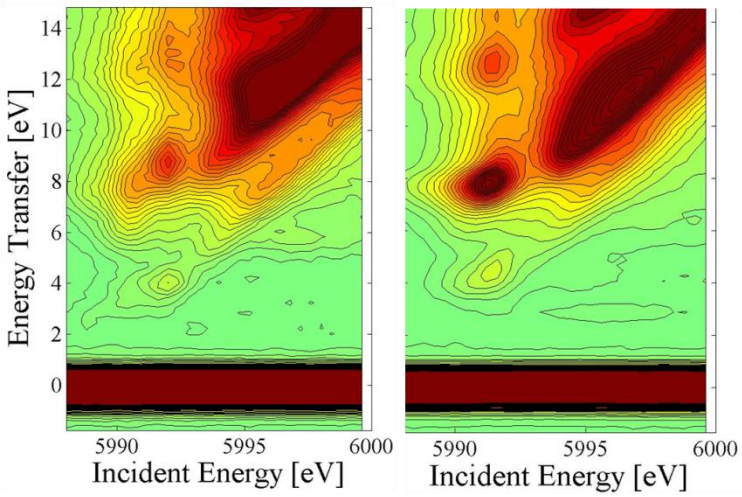

***Figure 2**. A comparison between the Valence to Core (VTC) RXES maps of sample 9) and 10).*

Part 2. In order to use all the available shifts, we also tried to study other important Cr-based systems (that we took with us for precaution): 9) to 12) that are promising systems in the fields of gas separation and purification, gas storage, drug delivery, optical material and catalysis. These new systems are Cr-based metallorganic framework. For them it was possible to collect XANES, Kβ satellite lines spectra (see **Figure 1**), RXES maps and we focused our attention on some important features arising in the map, collecting several resonant XES spectra (see **Figure 2**).

Part 3. The same approach was used studying the systems from 13) to 16) where XANES, Kβ satellite lines spectra, RXES maps were collected.

Acknowledgements

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