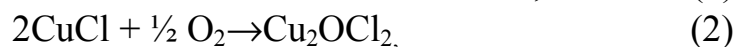
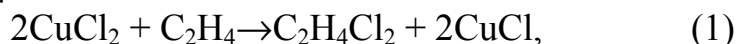




	Experiment title: CuCl <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> catalyst: a time resolved Cu-k edge XAFS study under catalytic conditions	<b>Experiment number:</b> <b>CH-1061</b>
<b>Beamline:</b> ID24	<b>Date of experiment:</b> from: 02 July 1997 to: 07 July 1997	<b>Date of report:</b> 29 August 2003
Shifts:15	Local contact(s): <b>Dr Sofia DIAZ MORENO</b>	<i>Received at ESRF:</i>
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Nowadays, almost all the world production of vinyl chloride is based on cracking of 1,2-dichloroethane. This compound, is produced oxychlorination of ethylene with hydrochloric acid and oxygen, catalyzed by  $\gamma$ -alumina impregnated with CuCl<sub>2</sub> according to the following three step mechanism [1]:



Variable concentration of other chlorides (mainly alkali or alkali earth chlorides), suggested by industrial production experience are also added to the  $\gamma$ -alumina/CuCl<sub>2</sub> system to make the catalyst more suitable for the use in industrial reactors.

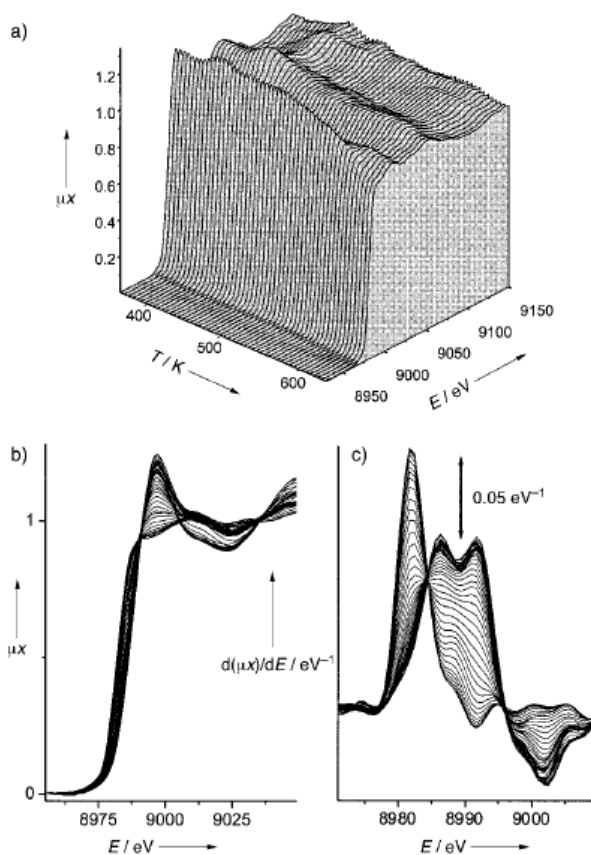
The experiments have been performed on ID24 by feeding a cell containing a self supported thin pellet of the catalyst with a diluted mixture of three reagents (C<sub>2</sub>H<sub>4</sub> : HCl : O<sub>2</sub> : N<sub>2</sub>). In the course of the experiment the temperature was increased from 373 to 623 K and then decreased again to 373 K. The gas output was analyzed by a quadrupole mass spectrometer. This has allow to investigate the wide range of temperatures which can be found in the different zones of the fixed bed reactors at different periods of catalyst lifetime. The study has been performed on the base catalyst and then it has been extended to a series of catalyst containing additives

The real-time monitor of oxidation state allowed by Dispersive XANES spectroscopy (see figure 1) coupled to the chemical analysis by mass spectroscopy has given for the first time a real picture of the behavior of the catalyst during the industrial process making available the study of the kinetic properties of the oxichorination reaction.

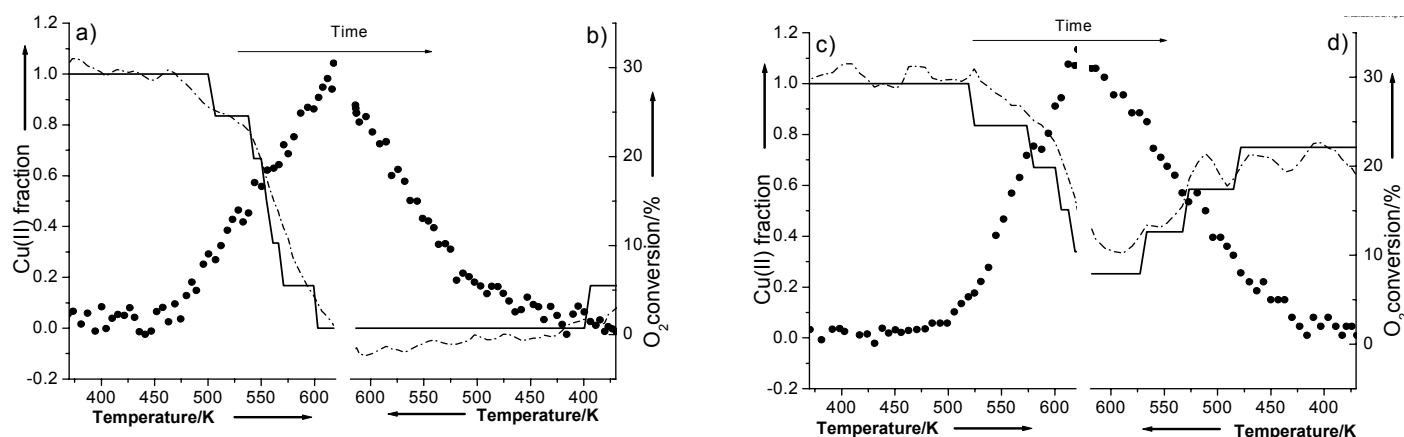
Two main result has been raised from this experiment:

The first one is that, the rate dermining step for the pure catalyst is step (1), as it is visible in Fig. 2a) and 2b) being the reaction activity (O<sub>2</sub> consumption) strictly correlated with the presence of the reduced phase.

The second one is that, repeating the experiment on catalysts added of other chloride, it has been found that some of the additives change the rate determining step of the catalyzed oxichlorination from the step 1 to the step 2, i.e. as shown in fig 2c and 2d for potassium. A first set of results of these experiments has been published in 2002 [5]



**Figure 1** Part (a): tridimensional XANES spectra (collected each 30 s) of Cu5.0 catalyst during the heating part of the experiment (from 373 to 623 K by 12 K min<sup>-1</sup>). Part (b) as part (a): front view. Part (c) corresponding derivative spectra. The presence of two isosbestic points in XANES (8990 and 9005 eV) and derivative spectra (8984 and 8995 eV) is noticeable. The Cu(II) → Cu(I) reduction can be appreciated by the decrease of the white line intensity part (a) and (b) and by the edge blue shift, more evident in the first derivative spectra part (c). A quantitative evaluation of Cu(I) and Cu(II) concentration has been obtained from the cross analysis of edge position and first derivative maxima.[3]



**Figure 2.** Part a) O<sub>2</sub> conversion (full dots) and Cu(II) fraction, obtained from edge shift (full line) and from the intensity of the d(μX)/dE maximum (dashed line), for Cu5.0 during ramp up. Part b), as part a) for the ramp down. Parts c) and d) as parts a) and b) for K3.6Cu5.0 catalyst.

[1]G. Leofanti, C. Lamberti, *et al.*, *J. Catal.* **2000**, *189*, 91-104; *J. Catal.* **2000**, *189*, 105-116; *J. Catal.* **2001**, *202*, 279-295; *J. Catal.* **2002**, *205*, 375-381.

[2] C. Lamberti, C. Prestipino, F. Bonino, L. Capello, S. Bordiga, G. Spoto, A. Zecchina, S. Diaz Moreno, B. Cremaschi, M. Garilli, A. Marsella, D. Carmello, S. Vidotto and G. Leofanti, *Angew. Chem. Int. Ed.*, **2002**, *41*, 2341-2344; *ESRF Highlights 2002*, pp. 37-38.

[3]C. Lamberti, C. Prestipino, *et al.*, *Phys. Chem. Chem. Phys.* **2003**, *5* (in press)