

Experiment Report Form



Experiment title: Investigation of copper surroundings and its oxidation states during reaction by EXAFS and XANES

Experiment number:
CH-3166

Beam line:	Date of experiment: from: 27-01-2011 to: 31-01-2011	Date of report: 11-11-2011
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Report:

The main aim of the experiments was to elucidate the oxidation states of Cu in $\text{CuCl}_2\text{-MCl}/\gamma\text{-Al}_2\text{O}_3$, $\text{CuCl}_2/\gamma\text{-Al}_2\text{O}_3$, and $\text{CuCl}_2/\text{UiO-66}$ catalysts during the oxychlorination reaction. The following objectives were set:

1. Observing the Cu(II)/Cu(I) ratio during reaction at different temperatures with respect to the dopant added, with fixed M/Cu ratio ($M = \text{K, La or Mg}$).
2. Effect of K/Cu ratio on the Cu(II)/Cu(I) ratio, as well as on the formation of K-Cu mixed compounds.
3. Effect of a different support for the oxychlorination reaction, here: “UiO-66” was used.

Experimental: A XAS study in transmission mode at Cu K-edge (8979 eV) was performed, with XRD as complimentary technique. The catalyst was loaded into a capillary, which was coupled to a gas feed system and a mass spectrometer (MS) for detection of feed and effluent gas composition. The gas stream passed through a water bath and was then further diluted with Ar before reaching the MS, in order for the HCl concentration to go below 2 %. The in-situ set up is showed in Figure 1.

The experimental procedure was as follows:

1. XRD and quick XANES spectra of the fresh catalyst were acquired at room temperature.
2. The catalyst was heated to 230 °C ($dT = 10^\circ\text{C}/\text{min}$) under He flow (35 ml/min). Quick XANES scans (2 minutes) were measured until the temperature reached 230 °C. Thereafter, EXAFS scans (2x 40 mins) were acquired.
3. The gas feed was switched to the reaction mixture ($\text{C}_2\text{H}_4 : \text{HCl} : \text{Air} : \text{He} = 56 : 20 : 23.8 : 60.2$ Nml/min, $T = 230^\circ\text{C}$. 56 Nml/min Ar was added after the reactor.). The majority of gas flow was fed in by-pass (due to too large mass flow controller capacity compared to the capillary size), while the maximum total flow through the capillary was 5-8 Nml/min. XANES scans (1 minute scans) were performed until a stable Cu(II)/Cu(I) ratio was observed. Then EXAFS scans (2 x 40 min) were acquired.
4. The temperature was ramped up to 280°C ($dT = 10^\circ\text{C}/\text{min}$) while acquiring quick XANES spectra. When the temperature was stable at 280°C, long EXAFS scans (2 x 40 min) and XRD was performed.
5. The temperature was reduced to 230°C. When the temperature was stable, 2 quick XANES scans and 2x 40 min EXAFS scans were acquired.

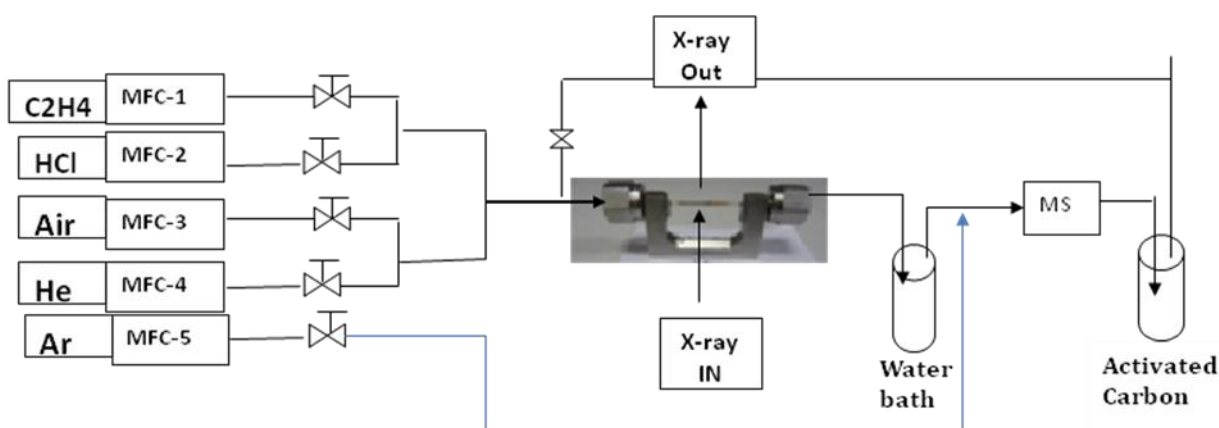


Figure 1: Schematic diagram of capillary reactor set up.

Results: XANES spectra for 3.1wt% KCl loaded onto 5wt% $\text{CuCl}_2/\gamma\text{-Al}_2\text{O}_3$ (K3.1Cu5.0) are reported in Figures 2-3. Figure 2 shows the spectra measured during heating under He, while Figure 3 shows spectra acquired under reaction conditions at 230°C. Comparison to reference spectra acquired for CuCl and CuCl₂, respectively, show that the sample remained in the Cu²⁺ oxidation state during heating (Figure 2). However, upon introduction of the reaction mixture at 230°C, Cu²⁺ was gradually reduced to Cu⁺ (Figure 3).

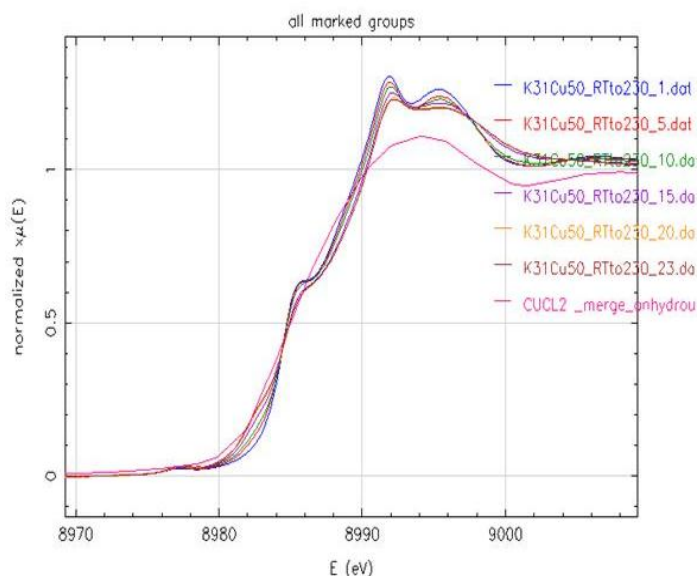


Figure 2: XANES spectra of K3.1Cu5.0 sample at Cu K-edge during ramping up temperature

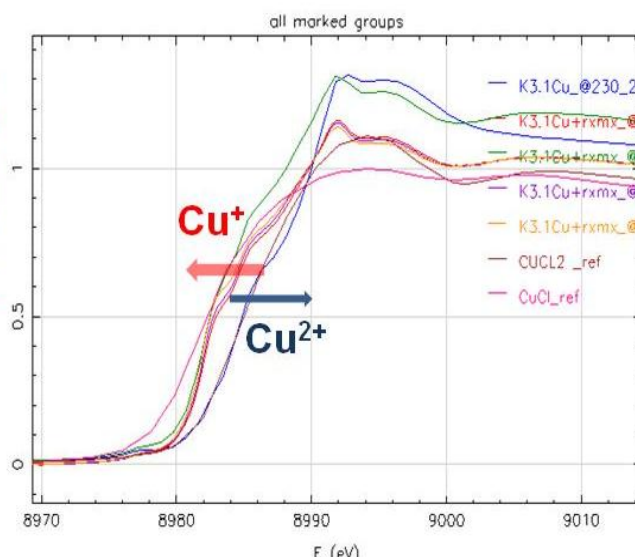


Figure 3: XANES spectra of K3.1Cu5.0 sample at Cu K-edge during interaction with reaction mixture at 230°C.

The information achieved by XANES data as exemplified in Figures 2-3, i.e. the relative fraction of Cu(II) and Cu(I) at different reaction temperatures, is vital for understanding the shift of rate determining step for different variants of CuCl_x catalysts. Another important information gained by this study (EXAFS spectra) was the disappearance of the Cu phase upon prolonged heating in all but the K-doped samples. Previous studies have indicated the formation of a mixed K-Cu-Cl phase, and work is currently in progress in the home lab to synthesise the mixed compound and test it as catalyst for the ethene oxychlorination reaction. MS spectra acquired during testing showed that the residence time in the capillary cell was too short to allow appreciable conversion of ethene, and this should be improved in future experiments at ESRF by applying a cell with a larger reaction volume.

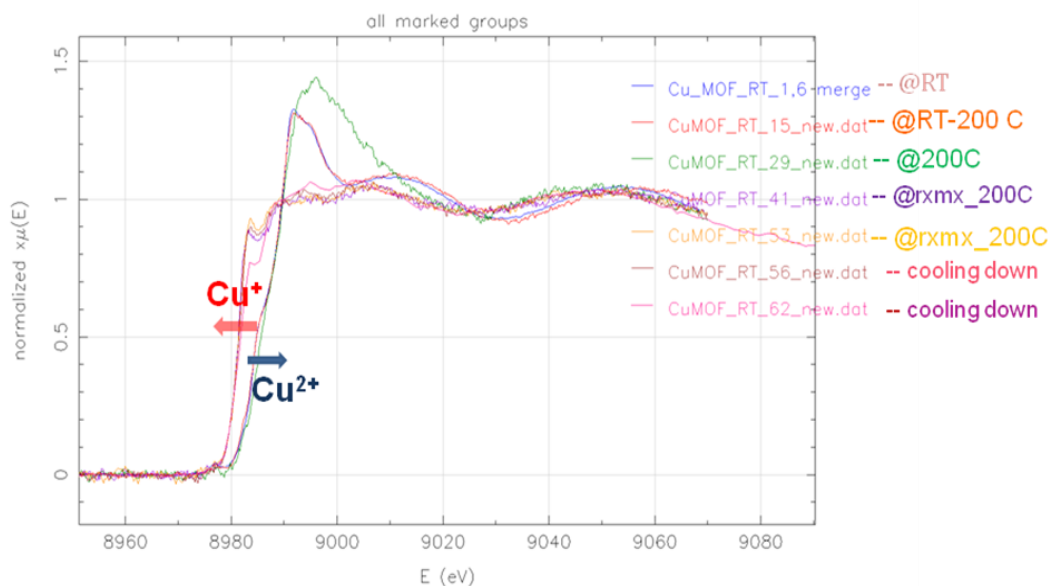


Figure 4: XANES spectra of Cu-MOF at CuK-edge during a catalytic experiment, where spectra were acquired at RT, at 200°C, with reaction mixture at 200°C, and during cooling to RT.

Finally, XANES spectra were acquired during heating, testing and cooling of a Metal-Organic Framework compound (MOF) with UiO-66 structure and CuCl_2 loading (Cu-MOF). Interestingly, the data obtained indicate that Cu^{2+} was reduced to Cu^+ upon introduction of the reaction mixture (Figure 4). XRD data (not shown) suggested that the material was unstable in the HCl-containing reaction mixture. However, the observation of accessible Cu species in the material bears promise that this material can be applied as catalyst for other reactions in a less corrosive environment.