	Experiment title:	Experiment
ESRF	**Experiment title:** *In situ* **XRD/XAS/Raman investigation of the oxidation states and phase transformations in copper based dehydrogenation catalysts**	**number**: 01-01-836
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Names and affiliations of applicants (* indicates experimentalists):

*Nina Hammer,

*Magnus Rønning

*Alexey Voronov

*Asmira Delic

*Jostein Bø Fløystad,

Department of Chemical Engineering, NTNU,

N-7491 Trondheim, Norway

Report:

Copper chromite catalysts have traditionally been used in industrial hydrogenation/dehydrogenation reactions, although the disposal of the spent catalyst represents an environmental problem due to the toxicity of chromite. Cu based catalysts supported on carbon show promising activity and selectivity for these reactions and could be a good candidate to replace the chromite [1]. However, the preparation of highly dispersed Cu on carbon is not trivial although a dispersion of 35 % has been reported in the literature [2]. Large amounts of oxygen containing groups on the carbon support improve the dispersion of Cu [3]. Characterisation results from earlier studies have shown that the nature of carbonaceous supports can exert a significant impact on not only the morphological characteristics, but also the chemical state of Cu particles at various stages of the reduction step [2]. However, pretreatment of the carbon with nitric acid to increase the amount of oxygen containing groups will give a higher dispersion of Cu on carbon but will have a negative effect on the selectivity in the dehydrogenation of isopropanol [3, 4]. Therefore, it may be more beneficial to use a second metal to improve the properties of Cu supported on carbon catalysts. Introducing a second metal such as Fe could improve the performance in several ways; i.e. by increasing the Cu dispersion, by

facilitating reduction of Cu at lower temperatures, or by altering the activity and selectivity. It is much easier to obtain a high dispersion of Fe than of Cu on carbon supports [5]. By first impregnating the surface of the carbon with highly dispersed Fe, the Fe may act as anchor sites for the subsequent depositions of Cu atoms and thereby increasing the Cu dispersion. Small particles may obtain different structural arrangements and show different catalytic behaviour than bulk metal. For copper hydrogenation catalysts, three different active phases have been proposed in the literature: Cu^+, Cu^0 and a mixture of Cu^+ and Cu^0 species [6]. Thus a challenge in such studies is not only the determination of the Cu dispersion, which requires the measurement of surface Cu atoms in the form of both metallic atoms and cuprous ions, but also the distribution of the oxidation states among the surface Cu atoms. Surface synergisms between Cu and its oxides have been demonstrated for the dehydrogenation of isopropanol over unsupported powder samples of Cu in various oxidation states [7]. Addition of a second metal such as Fe, Co or Ni to supported Cu catalyst systems have shown that the second metal increases the degree of reduction of Cu and a higher activity/selectivity can be obtained [8,9]. Earlier experiments show that an unusual high activity can be obtained by adding Fe to the Cu/carbon system. The activity increase can not be explained by a higher dispersion of Cu alone (not published). Also the turnover frequency increases dramatically. As there are many possible modes of interaction in supported bimetallic systems, powerful characterisation methods are needed to identify the significant contributions.

Experimental method:

XAFS were collected at the Cu K edge (8979 eV) and Fe K edge (7112 eV) in transmission mode. XRD was performed at $\lambda=0.5112$ Å in order to minimise the interference with the Cu and Fe K edges.

An in situ cell was used in order to combine the X-ray techniques and Raman. The cell set-up is shown in Figure 1. The cell consist of a steinless steel base and two lineare motion guides. A quartz capillary tube was used as a reactor and was fixed with swagelok fitings to the base. The catalysts bed was kept in place in the quartz tube by quartz wool plugs and heated by a vertical hot air blower. The catalysts were heated to 400°C with a heating rate of 2°C/min in 2 ml/min H_2 and hold for 4 hours, followed by cooling to 50°C in flowing He before the reaction mixture was introduced. The reactant was feed to the reactor by purging 10 ml/min He through a sparger containing iso-propanol at 20°C. The temperature was increased from ambient to 200°C and hold for 4 hours followed by cooling to ambient temperature. The gas outlet was monitored continuously by a mass spectrometer. XRD and EXAFS data were collected prior and after the reduction/reaction step as well as in between and continuously xanes scans of the Fe and Cu edge was performed during this process.
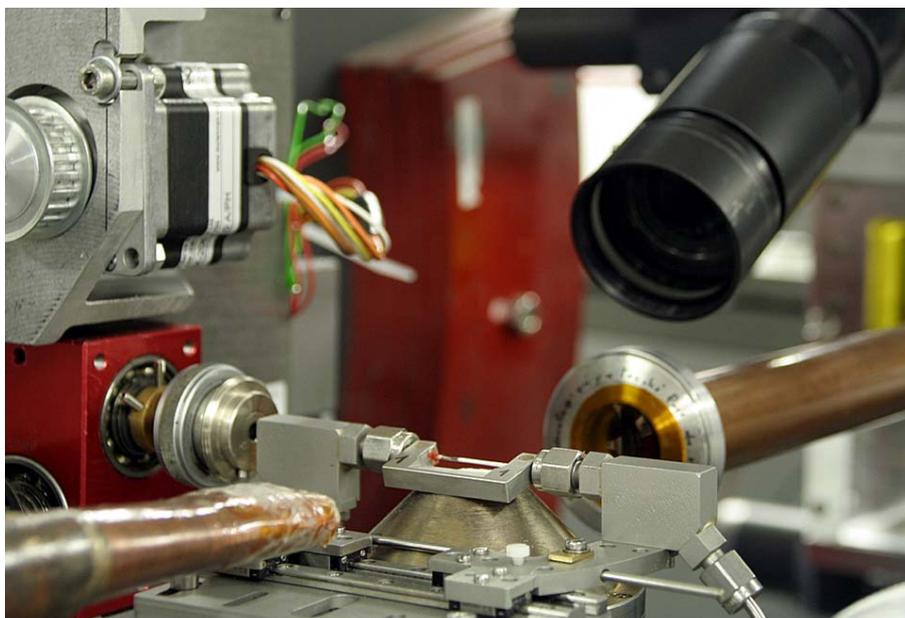
Figure 1: Reactor set-up for *in situ* XAS/XRD/Raman measurements

Results:

Characterisation of the as-prepared catalysts showed that Cu and Fe were present as Cu(II)O and Fe_2O_3. To follow the oxidation state of copper and iron the Cu and Fe k-edge XANES spectra were monitored durig the reduction step and reaction. The edge position related to the first inflection point gives information about the the oxidation state of the metals. The XANES of the Cu K-edge of CuO/Fe_2O_3 supported on hydrogen treated carbon during redcution in the temperature interval 110-190°C are shown in Figure 2.
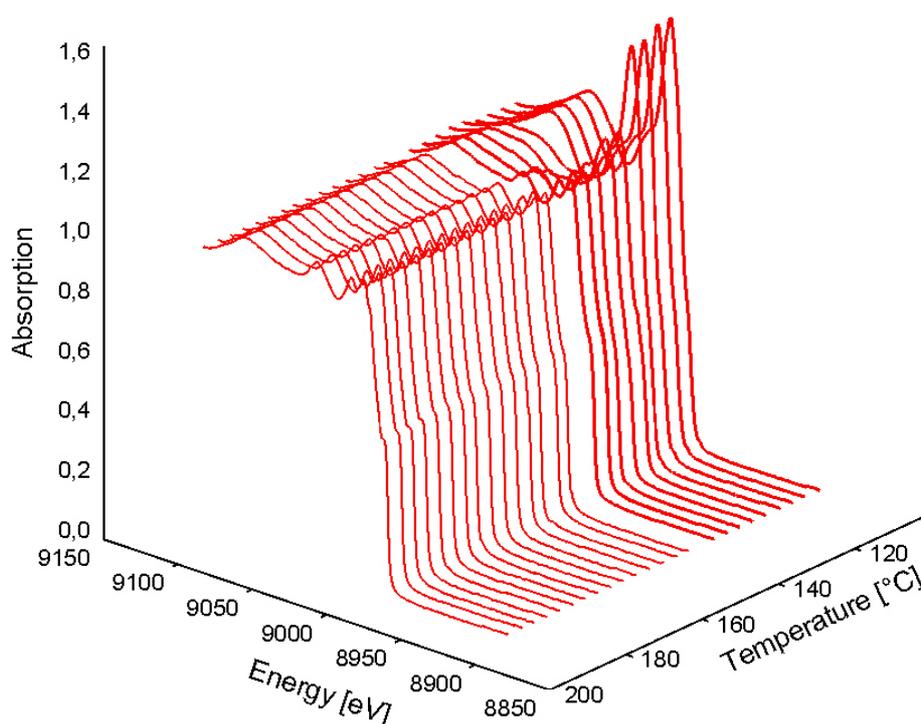

Figure 2: Temperature programmed reduction of CuO/Fe_2O_3 supported on carbon

The reduction profiles obtained from XANES show that the bimetallic catalysts started to reduce at 100°C. The reduction temperature for the bimetallic samples was lower compared with Cu supported on carbon in the absence of iron. The reduction of Fe_2O_3 started at higher temperature compared to Cu. Even after a reduction treatment at 400°C for 2 hours the XANES spectra revealed that Fe was not completely reduced. Linear combination fitting yielded an average composition of ~75%Fe(0), 25%Fe-oxide and 100%Cu(0) in the catalysts after the reduction treatment.

XRD data collected prior to the reduction of the catalysts showed none diffraction lines due to copper species. The absence of peaks related to copper may be attributed to highly dispersed Cu species on the surface or that the copper is amorphouse. However, very broad peaks of Fe-oxide could be observed. After the reduction strong reflections of Fe(0) and Fe-oxide could be identified and the 100% intensity peak for Cu(0) could be observed as a shoulder on the right side of Fe peak.

The activity measurements reveal that a conversion of 100% is reached at 200°C with a selectivity towards acetone of 80%. The diffraction lines became more narrow during the reaction likely caused by a higher crystallinity. However, comparison of diffractograms at the begin and after the reaction reveals that no structural and/or phase changes can be observed during the reaction.

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