

Fluorescence EXAFS for the *in situ* study on the state of promoters in catalysis

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The fluorescence EXAFS (FLEXAFS) technique has been combined with an *in situ* cell and on-line gas analysis. For this purpose a seven-element silicon drift detector has been used, which has high count rate capabilities and can be operated at room temperature. The potential of this technique is shown by the study of the state of copper promoter atoms in Fe-Cr based high temperature shift (HTS) catalysts. The FLEXAFS measurements revealed that Cu (0.17 – 1.5 wt%) is present in the metallic state under working conditions of the catalysts but easily re-oxidizes upon air exposure. The reduction behaviour of copper depends strongly on the copper concentration and the pre-treatment, i.e. if the catalysts have been calcined or used in the HTS reaction. For used catalysts, a Cu(I) phase was detected as intermediate during reduction. Its stability was especially high at low copper concentration.

Keywords: fluorescence EXAFS, XAFS, silicon drift detector, *in situ*, catalysis.

1. Introduction

Fluorescence EXAFS (FLEXAFS) instead of transmission EXAFS is the preferred technique when the concentration of the element of interest is low (Jaklevic *et al.*, 1977; Lytle *et al.*, 1984). For dynamic *in situ* studies, e.g. in the field of catalysis, high count rates are necessary. Conventional spectroscopy detectors are usually limited in counting rate because of their relatively high output capacitance (i.e. Gauthier *et al.*, 1996; Pullia & Bertuccio, 1996). Germanium and Si(Li) detectors permit high resolution spectroscopy, because they are relatively thick (up to 10 nm) and therefore have low capacitance. However, they must be cooled to liquid nitrogen temperature to minimize the leakage current. The recent development of multielement silicon drift detectors (Lechner *et al.*, 1996; Gauthier *et al.*, 1996) has shown that these allow sufficient count rates (150,000 cts/s) at low peak to background ratio (P/B=10⁵) even at room temperature.

The potential of this technique in catalysis will be demonstrated in the present study by results on the state of copper promoter atoms in Fe-Cr based high temperature shift (HTS) catalysts. HTS-catalysts catalyse the formation of hydrogen from CO and water (Bohlbro, 1969; Koechloefl, 1997), and the effect of copper is an increase in selectivity and activity (Andreev *et al.*, 1986). In order to obtain more information on the behaviour of Cu in the catalysts under *in situ* conditions, we have combined the FLEXAFS technique with an *in situ* cell and on-line gas analysis.

2. Experimental

The FLEXAFS experiments were performed at HASYLAB (DESY, Hamburg). The setup consists of a quartz capillary *in situ* cell (Clausen *et al.*, 1991) and a seven element multichannel

silicon drift detector (SDD, silicon chip by KETEK, Munich, electronics by HASYLAB). At the outlet of the capillary cell microreactor, on line gas analysis could be performed with a mass spectrometer (Clausen *et al.*, 1991; Grunwaldt *et al.*, 2000), which allows i.e. to record *in situ* temperature programmed reduction (TPR). The synchrotron radiation hits the capillary tube in a 30° angle in order to illuminate as much as possible of the sample. Moreover, in this way the silicon drift detector could be moved close to the cell. The signals of the silicon drift detector (each of the seven pixels of an area of 5 mm²) were amplified and recorded for each channel (for further details see Kappen *et al.*, 2000). Afterwards the spectra were dead-time corrected and summed up. The FLEXAFS scans were acquired around the Cu K edge (8980 eV) between 8800 and 9660 eV. Spectra were recorded within 30 to 60 minutes. Additionally, faster XANES scans in the fluorescence mode (8 – 10 min) were recorded under dynamic conditions.

Different Fe-Cr based catalysts, containing Fe and Cr in a molar ratio of about 10:1, have been investigated. The first series of catalysts were promoted with 0.17 wt% Cu (catalyst A) and 1.0 wt% Cu (catalyst B), respectively, and had been used under HTS conditions. The dry feed contained about 18% CO, 12% CO₂, 70% H₂ and steam was added to give a steam-to-dry gas ratio of 0.7. The catalysts were treated for 1000 h at HTS conditions. According to X-ray powder diffraction and Mössbauer studies, the main phase is a chromium substituted magnetite (Fe_{3-x}Cr_xO₄). Copper phases could not be detected by X-ray diffraction.

Additionally, two catalysts with 1.0 wt% Cu loading (catalysts C) and 1.5 wt% Cu loading (catalyst D) have been investigated. They were calcined prior to the characterization and had not been used in the HTS reaction. Hence, they contained mainly Fe(III) containing phases. All catalysts were reduced *in situ* in a 2% H₂/N₂ gas mixture saturated with water (3%, total flow of about 2 Nml/min, linear heating ramp of 1.5K/min).

3. Results and discussion

Figure 1 shows the multichannel analyzer spectrum of the samples A and B, containing 0.17 wt% Cu and 1.0 wt% Cu. The fluorescence lines of Cu_{Kα} and Cu_{Kβ} at 8.04 keV and 8.91 keV,

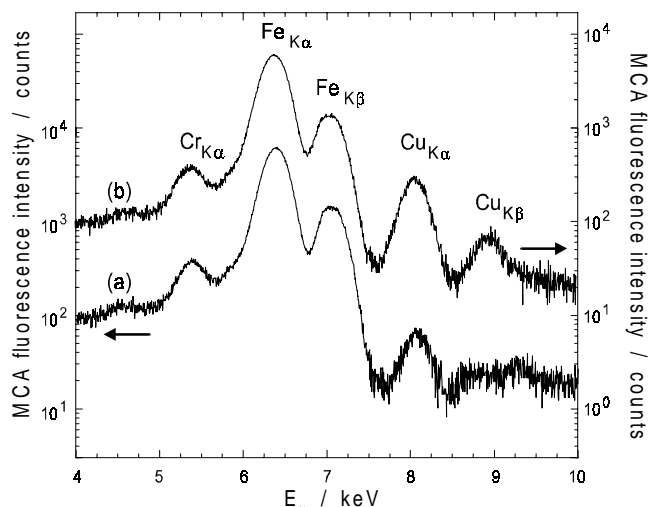


Figure 1 Multi-channel analyzer spectra: (a) 0.17 wt% Cu (catalyst A); (b) 1.0 wt% Cu (catalyst B) in Fe-Cr based HTS catalysts ($E_{\text{excit.}} = 12700$ eV).

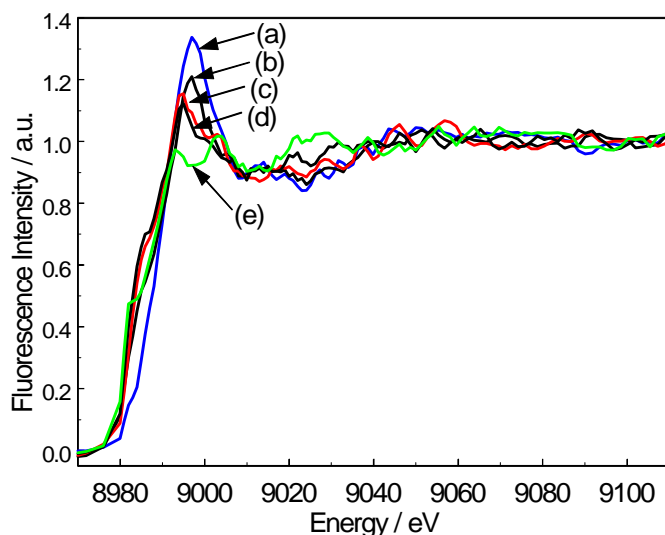


Figure 2
Selected *in situ* FLEXAFS scans at (a) 323 K, (b) 423 K, (c) 523 K, (d) 623 K, (e) 753 K at the Cu K-edge during the reduction, 0.17 wt% Cu (catalyst A).

respectively, are well separated from the other lines of Cr_K at 5.4 keV, $\text{Fe}_{K\alpha}$ at 6.4 and $\text{Fe}_{K\beta}$ at 7.06 keV, despite the low copper concentration and the quite heavy matrix. This makes FLEXAFS

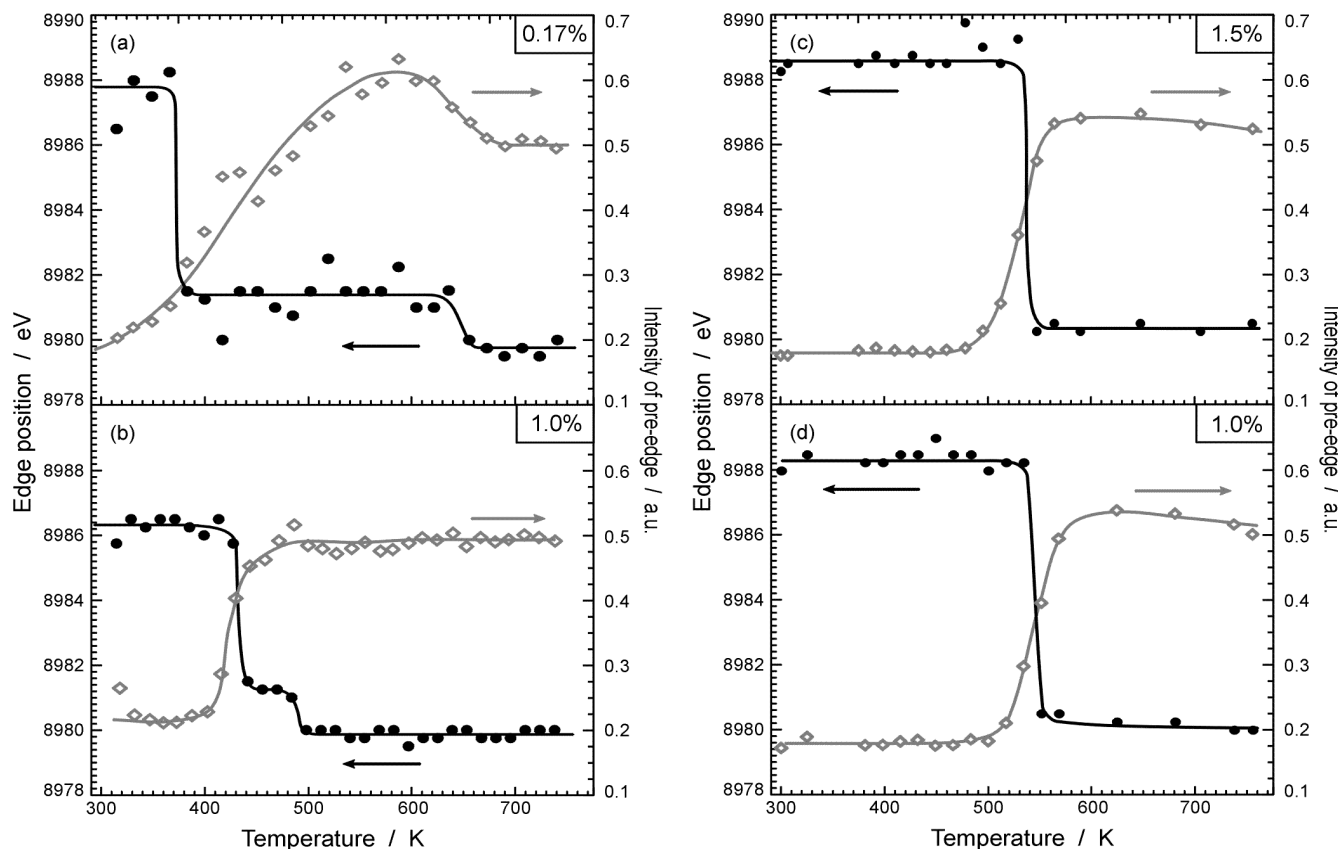


Figure 3
Cu K-edge energy and the intensity of the Cu-pre-edge as function of the reduction temperature in HTS catalysts: (a) 0.17 wt% Cu promoted catalyst (catalyst A, used in the HTS-reaction); (b) 1.0 wt% Cu promoted catalyst (catalyst B, used in the HTS-reaction); (c) 1.5 wt% Cu promoted catalyst (catalyst D, calcined); (d) 1.0 wt% Cu promoted catalyst (catalyst C, calcined).

studies feasible.

The analysis of the fluorescence XANES spectra revealed that copper is present as Cu(II) in all catalyst samples. In catalyst A and B copper has been oxidized due to air exposure after the HTS reaction, because, when the samples were reduced by heating to 753 K in the 2% H_2 /2% H_2O / N_2 gas mixture, copper was reduced to the metallic state. The *in situ* reduction is shown in Figure 2 where selected *in situ* FLEXAFS scans of the 0.17 wt% Cu promoted sample around the Cu K-edge are depicted.

While transmission EXAFS of catalyst A would result in a jump height of less than 0.002 at optimal conditions (with a pellet at an adsorption length of $\mu\text{-d} = 1.5$), sufficient statistics can be obtained with FLEXAFS (Figure 2). Additionally, one has to consider that the amount of sample is smaller in case of these *in situ* studies and only short scanning times were used (8 – 10 min).

In trace (e) of Figure 2 a pre-edge and oscillations, typical for the Cu(0) state, are found. Comparing the *in situ* XAFS data to reference spectra of CuO, Cu_2O and Cu, one can conclude that the reduction occurs in two steps via a Cu(I) species. In order to describe this intermediate step in more detail, the height of the pre-edge peak and the edge energy are depicted in Figure 3a (0.17 wt% Cu, in the HTS reaction used catalyst A), Fig. 3b (catalyst B), Fig. 3c (catalyst D), and Fig. 3d (catalyst C) depict the corresponding edge position and intensity of the pre-edge in dependence of the reduction temperature of the other 3 catalysts. One can see from the change of the edge energy in Figure 3a that the reduction from Cu(II) to Cu(I) occurs between 380 and 420 K

in catalyst A, whereas the final reduction from Cu(I) to Cu metal takes place at much higher temperatures (670 K) for this catalyst with the low Cu loading. Note also, that the whiteline decreases in two steps (see e.g. Fig. 2: from trace (a) to (b) and from (d) to (e)), indicating that an intermediate copper oxidation state is present. Similarly, the intensity of the pre-edge exhibits a maximum (see Figure 3a) as one would expect if there is a Cu(I) intermediate. The pre-edge band is due to the "1s-4p_z" atomic transition, which occurs when Cu(I) is in planar or linear geometry (Kau *et al.*, 1987; Yamashita *et al.*, 1996). However, the change is not as abruptly as in case of the edge energy shift. This can be interpreted as a process where the valence state of Cu sharply changes, whereas the symmetry around Cu only slowly changes to linear or planar geometry with more intense "1s-4p_z" transition. In case of higher loadings the reduction of Cu(II) to Cu(0) occurs much faster (catalyst B, Fig. 3b) and only in a small temperature interval there seems to be a stable Cu(I) phase (420 – 470 K).

The reduction of the calcined catalysts C and D is significantly different from catalysts A and B that have been used under HTS conditions. The reduction first starts at 520 K and there is no indication of a stable Cu(I) phase. Moreover, the simultaneously performed MS-analysis revealed that there was significant hydrogen consumption due to the reduction of the Fe(III) containing phases to the chromium substituted magnetite phase. The reduction of the Fe-Cr matrix started at about the same time as the reduction of copper. The results are summarized in Table 1 and no reduction of the Fe-Cr matrix has been found in case of catalyst A and B, because Fe(III) has been reduced to the magnetite phase under HTS conditions and the amount of Cu is too small to result in a significant signal in the TPR spectrum.

Table 1

Observed transformation of Cu(II) to Cu(I) and Cu(0) with FLEXAFS and reduction temperature T_{red} of the matrix (TPR)

Catalyst	T _{red} (Cu(II) to Cu(I)) / K	T _{red} (Cu(I) to Cu(0)) / K	T _{red} of the Fe-Cr matrix / K
A	390	670	already reduced
B	420	470	already reduced
C	520	520	530
D	520	520	530

From the reduction at 520 K of the calcined catalysts C and D, we conclude that copper in these catalysts seems to be more strongly bound to the matrix. Therefore these catalysts reduce later than the copper in catalyst B, which has once been reduced before. Hence, one can speculate that copper migrates out of the spinel phase of the catalyst during reduction. It is also well known from literature that CuO can easier be reduced than CuCr₂O₄ (Severino *et al.*, 1998).

The reduction behaviour of catalyst A shows furthermore that copper in small concentrations can either be stabilized on the surface or in the Fe-Cr matrix. Normally, the reduction of Cu(II) in hydrogen proceeds quickly and no intermediate phases can be found (cf. Clausen *et al.*, 1993). Only when using piezo-QEXAFS with a sampling time of 4.45 s/spectrum, indication for an intermediate Cu₂O phase has been found in case of CuO/ZnO/Al₂O₃ catalysts (Als-Nielsen *et al.*, 1995). However, in the present study the Cu concentration is lower and the enhanced stability in sample A (0.17 wt% Cu) could therefore be due to hindered copper crystal formation. Very recently, a two-step reduction of copper has also been reported (Yamaguchi *et al.*,

2000) when copper is incorporated into the channels of ZSM-5 zeolite, which supports this interpretation.

4. Conclusions

In the present study the fluorescence XAFS technique with a silicon drift detector (SDD) has been combined with an *in situ* cell and on-line gas analysis. The example illustrates that this technique can provide unique information of the structural properties of promoters in catalysis under working conditions. The SDD is advantageous for this application because it can record spectra in a sufficient short time scale. Thus it will be of general interest in catalysis and other fields, where the element of interest is present at low concentrations, e.g. noble metal catalysts, promoters and poisons. Further studies are presently in progress to apply this technique to other systems.

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