Report: Beamtime 01-01-748

"Serving the community; Integrated MSc training at SNBL"

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Several individual MSc projects are included in this project, all based on our work on structures of extraneous metal-containing zeotypic materials and the mechanisms behind their catalytic activity in deNOx processes. These results reveal information regarding the mechanisms of the chemical processes involving the incorporated metals. This depends on a number of factors including the supports and the method of introduction. Results will, combined with catalytic conversions, give an insight to possible active sites and mechanism. We include here some results from XANES and EXAFS studies on the interactions of the lower energy metals Ti and Cr incorporated into AlPO-5, in situ studies on variations in the copper oxidation states in ion-exchanged AgCu:Y and size determination of gold nanoclusters on zeotypic supports. We also succesfully collected in-situ XAS/Raman on CrAPO-5 to monitor the behaviour of chromium during the selective catalytic reduction of NOx with propene. Unfortunately it was not possibly with our current setup to carry out in situ measurments on the low energy elements titanium and vanadium.

1. XANES and EXAFs analysis of TAPO-5

A titanium incorporated aluminiumphosphate, TAPO-5, was synthesised and the sample characterised by XAS to reveal the local environments around the metal. Athena and excurve was used for analysis of the XANES and EXAFS respectively. XANES spectra of the calcined and uncalcined TAPO-5 compared to model compounds Ti-foil, anatase and rutile (Figure 1) shows that anatase is formed during the crystallisation process of TAPO-5.
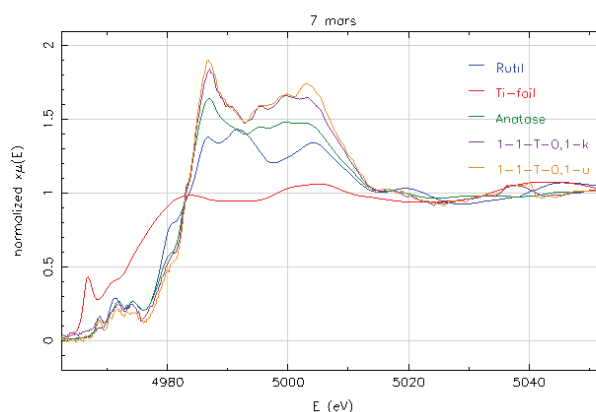

Fig. 1 XANES spectra of uncalcined and calcined TAPO-5 compared to models compounds.

The Fourier Transform of the calcined TAPO-5 is shown in figure 1. The multiplicity of the first shell, a Ti-O bond at 1,994Å, was 2,6. The second shell was fitted to 1,9 Ti…Ti distances at 3,071Å, whereas the third shell had a multiplicity of 2,2 and was fitted to a Ti…Ti bond distance of 3,921Å.
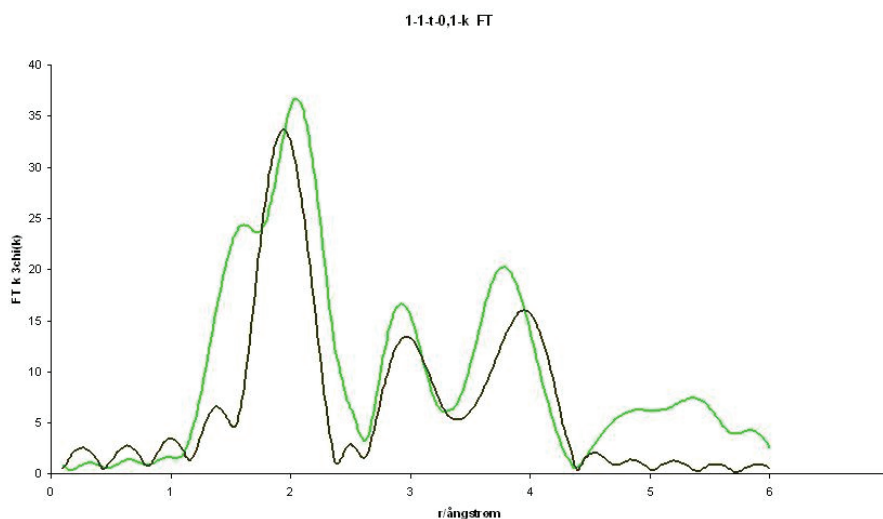

Fig. 2 Fourier transform of calcined TAPO-5

Both the uncalcined and calcined sample of TAPO-5 showed great resemblance to anatase but the multiplicity of all the shells was lower than for the bulk phase. This suggests that anatase is present as nanoparticles, possibly located within the AlPO-5 channels. The size of the anatase particles will be further investigated.

2. XANES and EXAFs analysis of CrAPO-5

EXAFS-data was recorded for the as-synthesized and calcined samples of CrAlPO-5 at room temperature in air. Comparison of uncalcined and calcined sample with models for Cr^{6+} and Cr^{4+} is shown in Figure 3. Results show that chromium is oxidized when calcined. The results indicate that chromium is not incorporated into the framework, but rather occupies extra-framework sites. Information obtained from the fit results also supports the theory for the color changes.
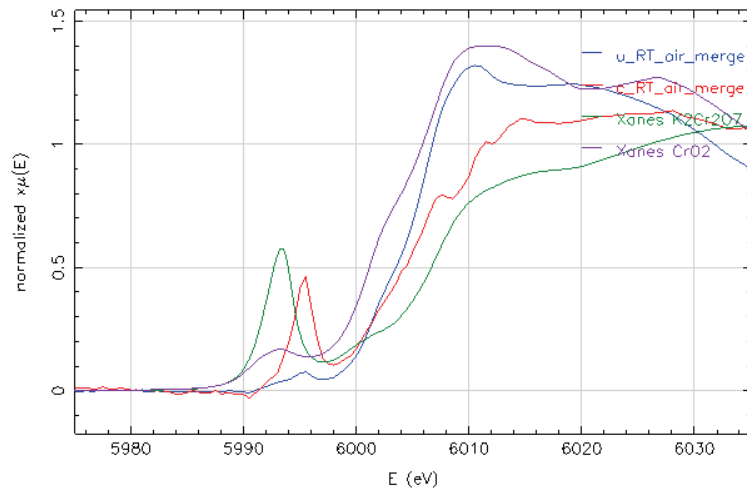
Fig. 3 Comparison of uncalcined and calcined samples with models of Cr^{4+} and Cr^{5+}.

XANES-data was recorded for calcined CrAPO-5 at various temperatures with propene/O_2-gas flowing through (Figure 4). Data for the sample in NO/O_2-flow is shown in Figure 5.
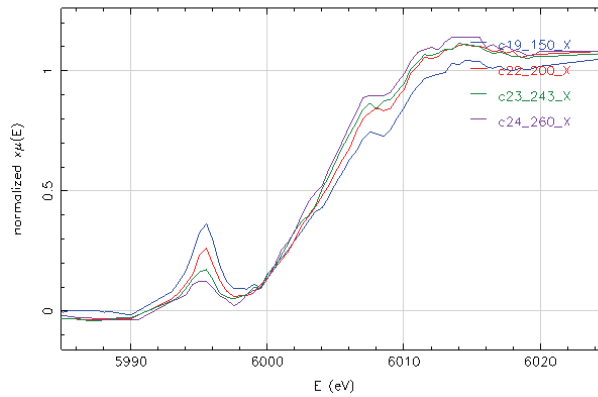

Fig. 4 XANES for calcined CrAlPO-5 in propene/O_2, varying temperature
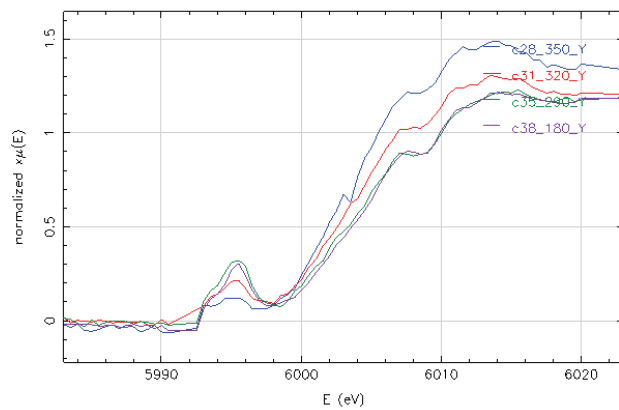

Fig. 5: XANES of calcined CrAlPO-5 with varying temperature and NO/O_2- gas flow

These results show that chromium(VI) is reduced when temperature increases in propene/O$_2$-gas and then reoxided in NO/O$_2$. This is evidence that chromium is reversibly oxidized/reduced and may be used as a catalyst in a reduction/oxidation reaction.

3. Variation of copper oxidation state during removal of NOx with hydrogen for AgCu:Y

Normalized Cu XANES of AgCu:Y during heating in helium to 150°C and then in hydrogen to 450°C, is shown in Figure 6. A clear shift towards lower edge energies is observed, supporting the reduction of copper(II) to copper(I), and possibly also metallic copper.
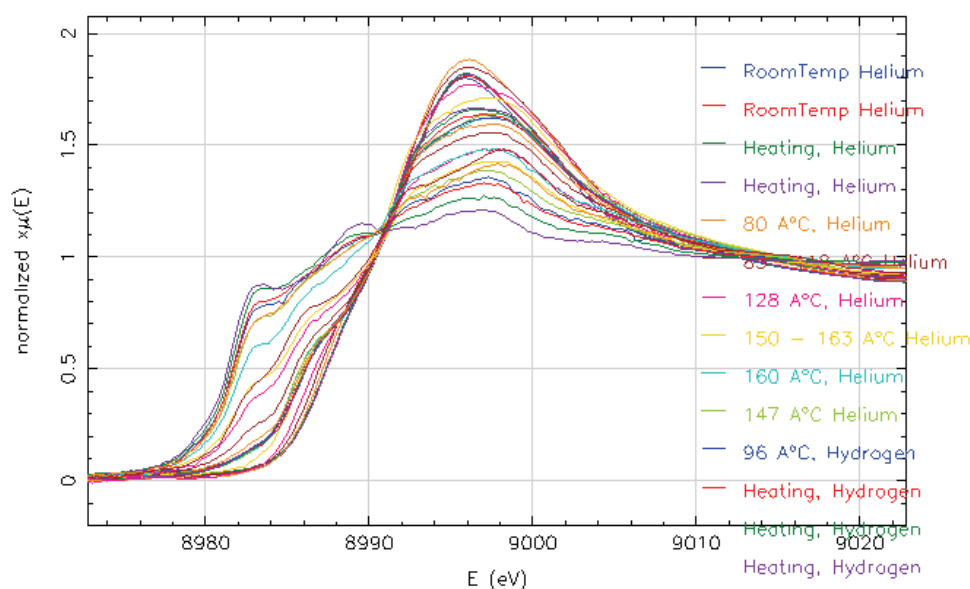

Fig. 6 Normalized Cu XANES spectra for the in-situ measurement

Using the linear combination fit in Athena, elementary copper and Cu(I) are formed during reuduciton in hydrogen (Fig. 7). The appearance of pre-edge shoulders in the XANES spectra is assigned to reduction of copper in the sample during hydrogen treatment. It's clear that introduction of NO changes the oxidation state of copper, and further pass-through of the gas oxidizes the copper even more.
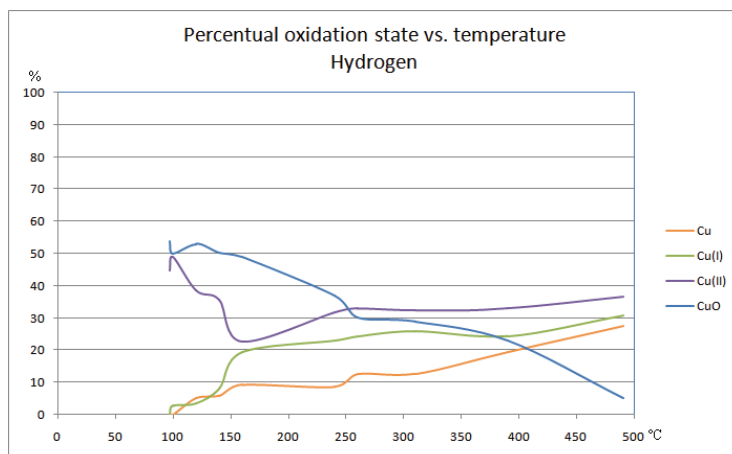
Fig. 7 Distribution of copper oxidation states as a function of temperature during the in-situ measurement

4. Gold nanoparticles on zeotypes

As synthesized and calcined gold incorporated SAPO-5 (AuSAPO-5_24h and AuSAPO-5_24C) were compared to an Au(0) foil and an Au(I) source to determine the Au valence state. The normalized XANES and Fourier Transform for the two samples compared to the curves for Au(0) foil and Au(I) source which was used as models are shown in Figures 8 and 9 respectively.
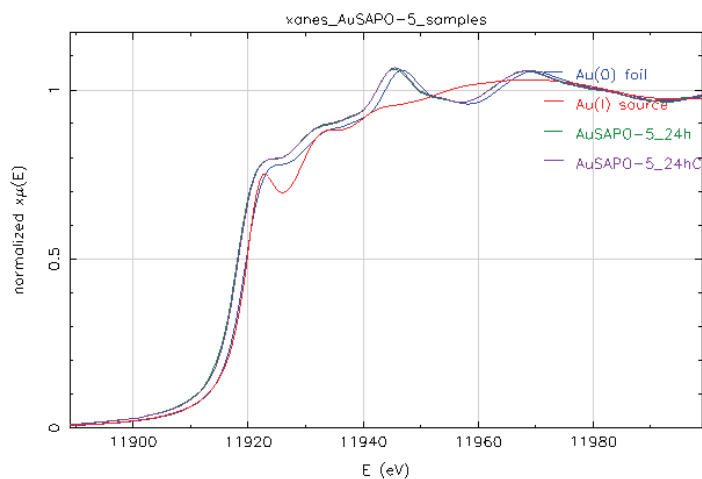

Fig. 8 The normalized XANES for the AuSAPO-5 samples compared to the models
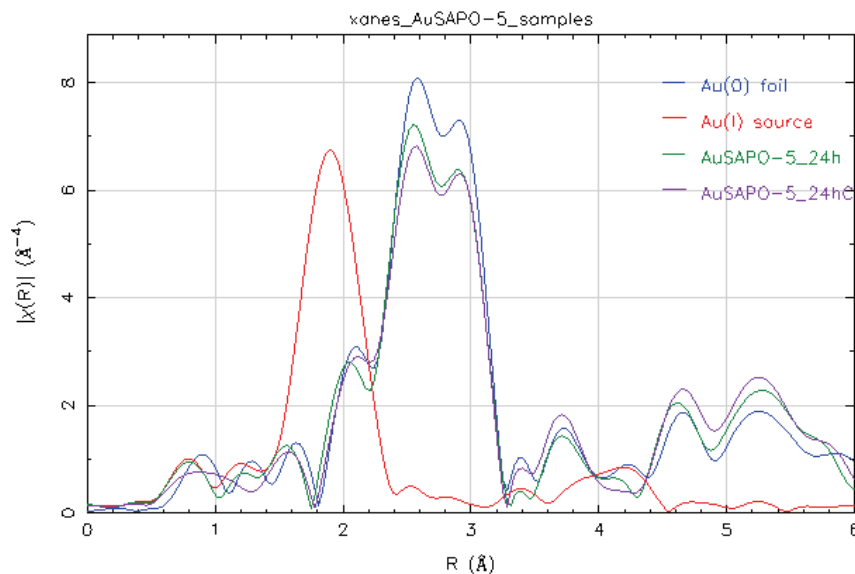
Fig. 9 Fourier transformation for the AuSAPO-5 samples

The amplitude for the samples is much lower than the Au(0) amplitude which can indicate that the Au particles are smaller, or that the ion exchanged sample contains a mixture of monovalent and metallic gold. By comparing the multiplicity from Excurve analyses of the samples with previously reported results we obtain the cluster sizes shown in Figure 10.
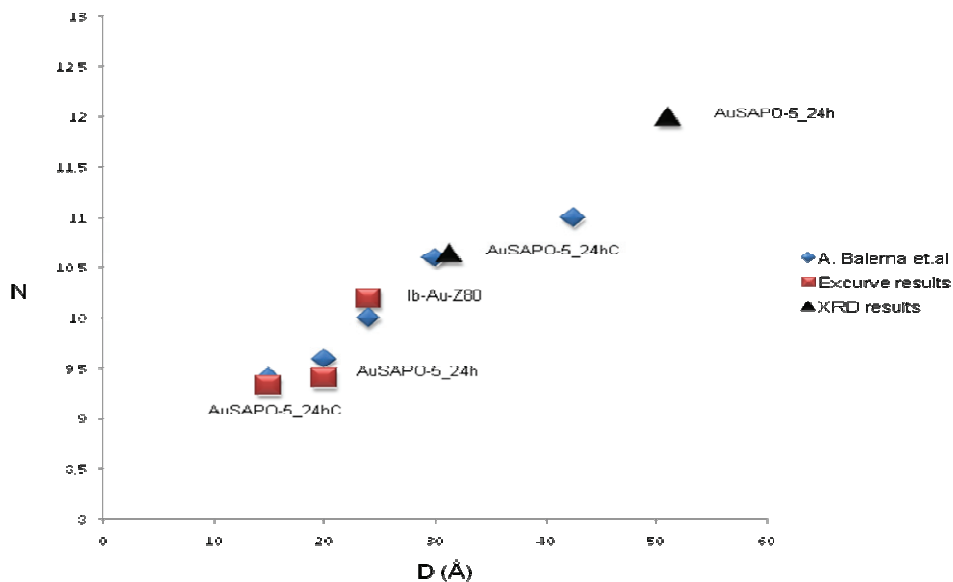

Fig. 10 Gold cluster particle sizes.

From the figure we see that both Excurve and XRD analyses conclude that the uncalcined sample contains gold particles of a larger size than what the calcined sample does.