ESRF	**Experiment title:** ***In situ* XRD/XAS investigation Pd-Cu/C catalysts in the catalytic reduction of nitrates**	**Experiment number**: 01-01-851
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Report:

Natural nitrate levels in groundwater are generally very low (<10 mg/L), however concentrations higher than 50 mg/L are frequently observed in several parts of Europe. The pollution is related to the over-usage of fertilisers in agriculture as well as waste effluents from certain industries. The nitrate compounds have been proven to be harmful for mammalian organisms. Once nitrates absorbed in the body of humans the nitrate will be partially reduced to nitrite before transformed to ammonium. Nitrite is a hazardous substance which can cause what is known as 'the blue baby syndrome' in humans and it is also a precursor to carcinogenic nitrous amines. Nitrate ions are easily distributed to groundwater sources since most nitrate salts are soluble in aqueous medium which may lead to surpassing of the legal limit for the water source. The European legislation has established the admissible concentration of nitrates in drinking water to 50 mg/L due to these harmful effects.

There are three main types of processes that can be used for removal of nitrates; physical-chemical, biological and catalytic [1]. Biological and physicochemical treatments allow effective removal of nitrates but have several economical and ecological disadvantages. Catalytic reduction is a promising route for destruction of pollutants in water. This process demands catalysts with high activity and stability since the reaction temperature will be set by the water source, and by possible unwanted leaching of catalyst metals to the water. The drawback of the reaction is the generation of ammonia as a by-product due to over-reduction. Hence, high selectivity towards nitrogen is required to be sure that the ammonia concentration does not exceed the legislation limits for drinking water. The most effective catalysts that have been reported are the bimetallic catalysts consisting of a noble metal (e.g. Pd, Pt, Ru, Re) that can easily chemisorb hydrogen and a transition metal as a promoter (e.g. Cu, Si, In) [2]. The nitrate reduction is believed to occur over binary catalyst sites or over transition metal sites in close connection with the noble metal. The role of the noble metal is bi-functional; to recover the activity of the promoter by hydrogen activation and to convert nitrite into nitrogen or ammonia [3]. Recent results suggest that multi-walled carbon nanotubes ar promising support for bimetallic catalysts [4]. It is known that the support is not active in the reactions and that the monometallic catalysts (both Cu and Pd) are not active for nitrate reduction. Pd monometallic catalysts are active for nitrite reduction, whereas Cu monometallic catalysts are only marginally active. In Pd-Cu catalysts, the role of the promoter metal (Cu) is to reduce nitrate according to a redox reaction, leading to nitrite and to an oxidized form of the promoter metal, which is reduced by hydrogen adsorbed on the noble metal. Then, nitrite migrates from the promoter metal to palladium sites, where it is further reduced to the end-products (nitrogen or ammonium).

Although the possibility of reducing nitrate ions in water with hydrogen in the presence of noble metals has been demonstrated to be an attractive route there is little information about the active sites and causes of deactivation with time on stream. However, some results from fresh and used catalysts are reported. X-ray photoelectron spectroscopy and XRD results on fresh and used Pd-Cu catalysts show contradicting results on the oxidation state (Pd(II) or Pd(0)) of Pd [5,6,7]. Corma *et al.* [5] also studied Cu together with Pd in the Pd-Cu system. Their XRD results did not show any peaks related to Cu due to low loading and relatively high dispersion. However, the XPS results indicated an increase in Cu^{2+} on the surface of the used catalyst. Consequently, more studies are necessary in order to obtain better understanding of the role of the metals during reaction.

Experimental method:

XAFS were collected at the Cu K edge (8979 eV) and Pd K edge (24350 eV) in transmission mode. XRD was performed at λ=0.5019 Å in order to minimise the interference with the Cu and Pd K edges.

A stainless steel cell, see Fig. 1, designed for both liquid- and gas phase reactions equipped with capton windows and carbon gasket was used for the experiments. The cell was heated by cartridge heaters located at the upper- and lower part of the cell and the power was provided by a power supply. The experiments were performed in two steps: First the catalysts were reduced by heating to 150°C with a heating rate of 2°C/min in 15 ml/min 5%H_2/He. The temperature was held for 2 hours prior to cooling down to ambient temperature in He. In the second step the liquid (see Fig. 1B) was continuously saturated by flowing

110 ml/min CO_2 and 110 ml/min 5%H_2/He through the solution before the gases were send to the exhaust system. The nitrate-containing water was pumped through the cell at a rate of 5 ml/min. The liquid went through a closed loop during the reaction. The reaction was performed at ambient pressure and room temperature.

XRD and EXAFS data were collected prior to and after the reduction/reaction step as well as in between. Continuous EXAFS scans of the Pd and Cu edges were performed during this process.

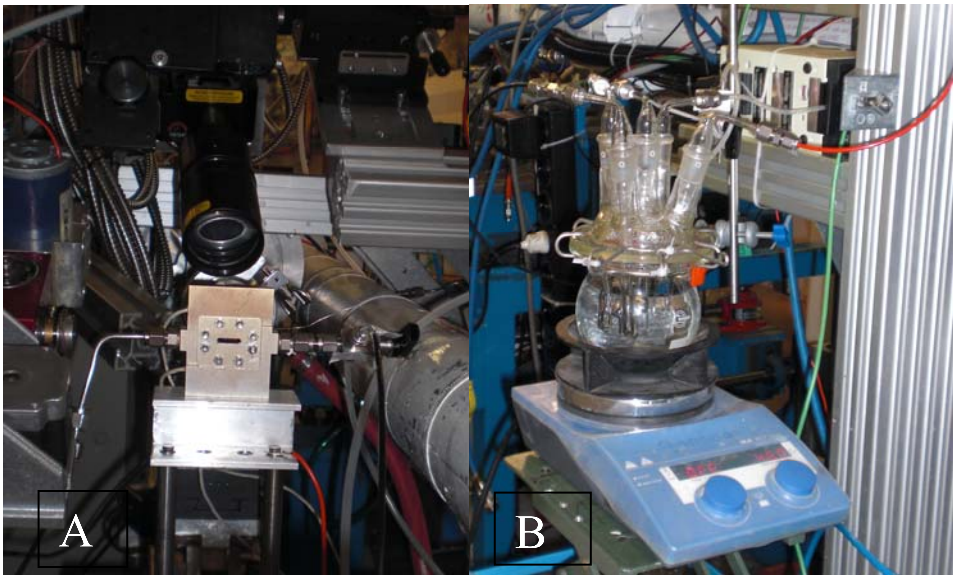

Figure 1: Pictures of the gas-/liquid *in situ* cell (A) and the liquid reactor (B) used for the reaction.

Results:

Characterisation of the as-prepraed catalysts showed that Cu and Pd were present as oxide. To follow the oxidation state of the metals the EXAFS spectra were monitored during the reduction. The shift of the absorption edge to lower energy corresponds to the reduction of the absorbing Cu atoms. The XANES at the Cu K-edge of Cu/Pd supported on carbon and Cu/Pd supported on alumina during reduction are shown in Figure 2. The reduction profiles obtained for the bimetallic catalyst, reveals that the reduction temperature of copper depends on the support. The intensity of the first inflection point of the Cu K-edge starts to decrease already at 25°C and the energy position is lowered for the catalyst supported on carbon. Compare to the carbon supported catalyst the reduction of copper supported on alumina starts at approximately 110°C and the rate is much lower. Therefore, will carbon as support reduce the risk of alloy formation between Pd and Cu due to relatively high reduction temperture.

The fraction of the different oxidation states of copper was determined by linear combination using Cu foil, CuO and Cu2O as reference models, respectively. Figure 3 shows the results for Cu/Pd supported on carbon obtained during the reaction and the last points show the results from exposing the catalysts to air.

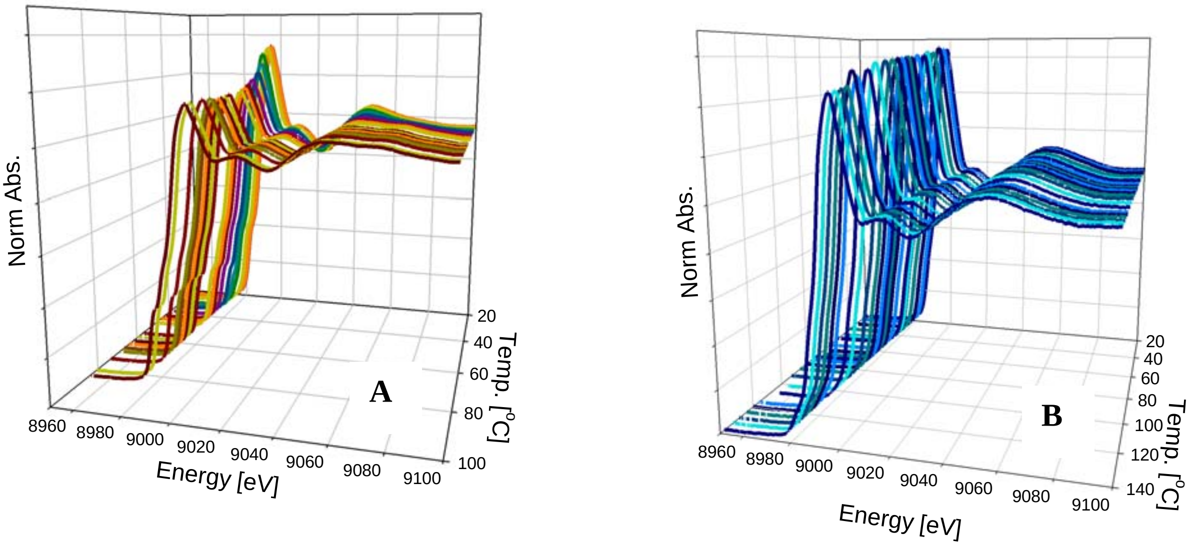

Figure 2: Normalised XANES spectra of CuO/PdO supported on carbon A) and CuO/PdO/ supported on alumina B) during reduction.

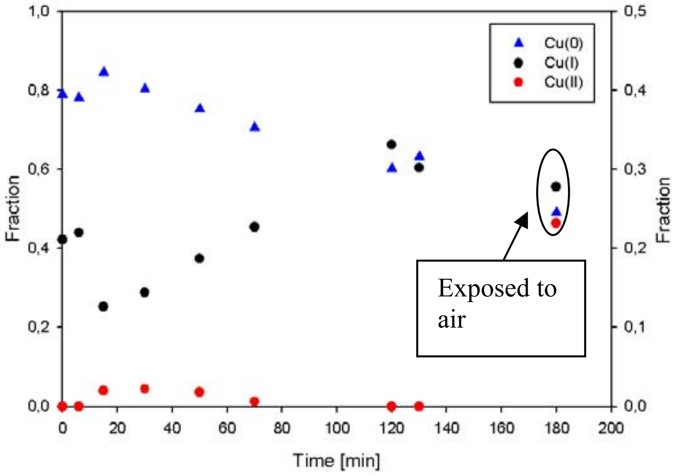

Figure 3: Changes in oxidation state of copper during the catalytic reaction of nitrates. The last points are the result from linear combination of the catalyst exposed to air after the reaction.

The results show that the main fraction of Cu is Cu(0) in the start. Thus, during the reaction the fraction of Cu(I) increases on the expense of the Cu(0). The fraction of Cu(II) is practically zero during the reaction and the oxidation to this state does not occur before air is introduced. These results prove that Pd is able to stabilise Cu in its lower oxidation state even when the catalyst is exposed to air.

References

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