

In situ XAS of Ir Black during the Selective Catalytic Reduction (SCR) of NO_x

E.A. Willneff¹, N. Weiher¹, C. Wögerbauer², M.M. Schubert², A. Baiker² and S.L.M. Schroeder¹

¹Institute for Chemistry, Free University of Berlin, Takustr. 3, 14195 Berlin, Germany

²Technische Chemie, HCI E 133, ETH Hönggerberg, 8093 Zürich, Schweiz

Currently used three-way catalysts do not effectively reduce NO_x under lean burn conditions, *i.e.* in the presence of high oxygen-to-fuel ratios. A significant source of undesirable NO_x emissions comes from modern Diesel engines, which operate under just these conditions. It has been suggested that NO_x control can be achieved by selective catalytic reduction (SCR) in the presence of an added reductant. Iridium based materials have shown promising results as catalysts for this process [1]. Recent work [2,3] has shown that the degree of oxidation and size of the Ir particles are important parameters in determining the overall activity of the catalysts. As a preliminary investigation into these findings we have characterized Ir black with X-ray absorption spectroscopy (XAS) during reductive and oxidative pre-treatments as well as during conditioning with a simulated exhaust gas mixture.

XAS measurements were carried out at the Ir-L₃ edge on beamlines X1 and A1 using a double crystal Si(311) monochromator. Higher order beam harmonics were rejected by detuning the second crystal monochromator to approx. 50% of maximum intensity. The pre- and post-sample ionization chambers were filled with a 50/50 mixture of Ar/N₂ and 100% Ar respectively. Measurements at X1 were also performed in the quick-EXAFS (QEXAFS) monochromator mode. The transmission cell was a modified plug-flow laboratory reactor that enabled in-situ XAS measurements to be taken under the same flow conditions as found in the activity tests in the laboratory. Ir black was diluted with BN at a 1:20 ratio for measurements. The catalyst bed contained 10 mg of the diluted sample.

Reductive pre-treatment in 5% H₂/He over 353-573 K was found to have little effect on either the oxidation state or long-range order of untreated iridium black. Both the height of the absorption edge, which is characteristic for the oxidation state of the absorbing element, as well as the in the fine-structure oscillations remained constant over the entire temperature range. The significant reduction in EXAFS amplitudes over the entire *k* range and overall damping of the fine structure features at the curve maxima (fig. 1) as compared to those of an Ir foil are characteristics indicate the presence of small particles. The coordination numbers for the first three shells were obtained by fitting the EXAFS over this range with single scattering paths generated by FEFF8 for an ideal Ir fcc lattice. We found that the coordination numbers were reduced to approx. 84%, 66% and 25% for

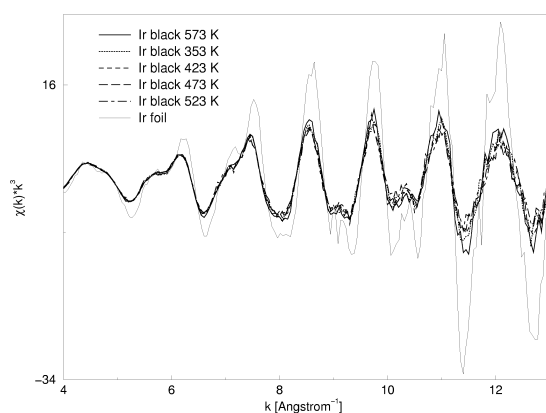


Figure 1: EXAFS of Ir black during reduction in 5% H₂/He over 353-573 K. Ir foil is included as a reference to demonstrate the overall decrease in amplitude due to the presence of Ir black particles approx. 3 nm in diameter.

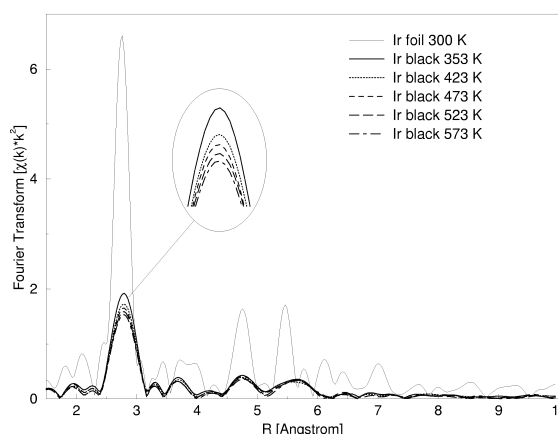


Figure 2: Fourier transforms of the EXAFS taken during the reduction of Ir black.

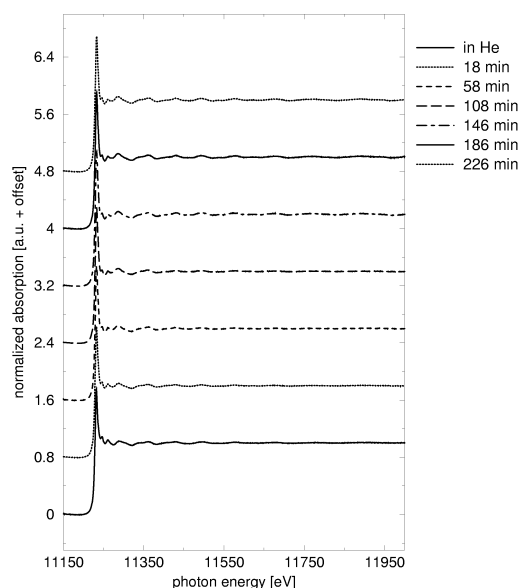


Figure 3: Normalized X-ray absorption spectra of Ir black during conditioning at 723 K. With time the EXAFS is seen to intensify pointing to sintering of Ir black.

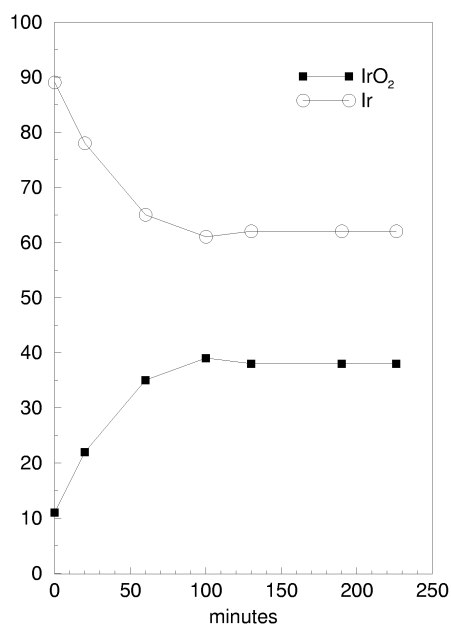


Figure 4: Composition of Ir black during conditioning as determined from fits to the XANES with a linear combination of IrO₂ and Ir reference spectra.

the 1st, 2nd and 3rd shell respectively of the values expected for Ir metal. Application of a relationship between the EXAFS-determined coordination number and the particle size [4] suggested that the particles are spherical and between 2.3 and 3 nm in size. These values were confirmed by a powder XRD line broadening analysis.

Following reduction, the sample was treated in a simulated exhaust gas consisting of 1800 ppm propene, 450 ppm CO, 8% O₂, 300 ppm NO, 1.5% H₂O, 10.7% CO₂ and He as a carrier gas with a total flow rate of 100 ml/min for 4 h at 723 K. Sintering and oxidation of the particles during treatment is apparent from the increasingly pronounced fine-structure and an increase in the white line intensity respectively (fig. 3). Fitting a linear combination of IrO₂ and Ir reference spectra allowed us to determine the oxide content as a function of treatment time (fig. 4). The maximum IrO₂ content of 40% was reached after ca. 1 h on-stream and was maintained for the rest of the 4 h period. This compares roughly with results reported in [2] of 30% IrO₂ following treatment in a similar reaction mixture.

Further *in situ* XAS measurements under reaction conditions are planned with the aim of gaining more insight into the relationship between oxidation state, particle size and catalytic activity of these Ir-based SCR catalysts.

References

- [1] T. Nakatsuji, Appl. Catal. B 25, 163 (2000)
- [2] C. Wögerbauer, M. Maciejewski, M. Schubert, and A. Baiker, Appl. Catal. B 34, 11 (2001)
- [3] C. Wögerbauer, M. Maciejewski, A. Baiker, and U. Göbel, Top. Catal. 16, 181 (2001)
- [4] R.B. Gregor and F.W. Lytle, J. Catal. 63, 476 (1980)