



Experiment Report Form

	Experiment title: Investigation of in situ nitriding in iron-based ammonia synthesis and decomposition catalysts.	Experiment number: CH-4585
Beamline: ID 26	Date of experiment: from: 10/11/2015 to: 16/11/2015	Date of report: <i>Received at ESRF:</i>
Shifts: 18	Local contact(s): Pieter Glatzel	
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Report:

The conversion of dinitrogen to ammonia is a process of fundamental biological and industrial importance. While the impact of the more than 100 year old industrial Haber-Bosch process is undoubtedly immense, the exact mechanism by which the heterogeneous Fe catalysts cleave the triple bond of dinitrogen remains unknown. The Nobel prize winning work of Ertl utilized idealized iron surfaces to put forth the idea that dinitrogen was absorbed as surface nitrides. However, despite decades of research the surface nitrides have never been observed in the industrial catalyst. The research conducted in our laboratory aims to detect these surface nitrides and to describe the interaction of the nitride with the iron surface. Toward this end hard X-ray probes are ideal, as they have the potential to be utilized under in operando conditions and applied to the working catalyst.

During our November 2015 beam time, we focused on an Fe LDH-based catalyst synthesized in the Schlögl laboratories at the MPI CEC, which may act as both an ammonia decomposition or an ammonia synthesis catalyst. During our ID26 beam time we were able to measure the K-Beta and valence-to-core X-ray emission spectroscopy of the calcined, reduced, spent catalyst after ammonia decomposition (at different temperatures) and spent catalyst after ammonia synthesis (in pure form and impregnated with KNO_3 : K3(impregnated, calcined, reduced), K4(calcined, impregnated, calcined, reduced)). In addition, we were

able to obtain RXES planes in the VtC region, which show clear indications of added selectivity from this approach (as will be detailed below).

Figure 1 shows the K-Beta mainline data for the calcined (cal), reduced (red) and spent catalysts (obtained from reactions runs at 350, 360 and 370 C). The mainline of the calcined sample is consistent with high spin iron in an admixture of Fe(II)/Fe(III) oxidation states. Upon reduction the Fe total spin is reduced site, consistent with $S=1$ d^8 alpha-iron. This apparent spin state persists following completion of the reaction (at either 350, 360 or 370 C). However the mainline shifts in energy, strongly suggesting that the product is no longer dominantly alpha-iron. Figure 2 shows the K-Beta mainline data for spent catalyst after ammonia synthesis (both in pure form (sy) and impregnated with KNO_3 at different stages of the preparation (sy_K3 and sy_K4, as detailed above)). The reduced catalyst is also shown for reference. Although the changes are subtle, there is a measurable decrease in the KB' feature at ~ 7045 eV in the spent catalyst impregnated with KNO_3 relative to sy or red. This suggests that the potassium impregnated spent ammonia synthesis catalyst is not simply the same bulk alpha-iron as observed in the reduced catalyst.

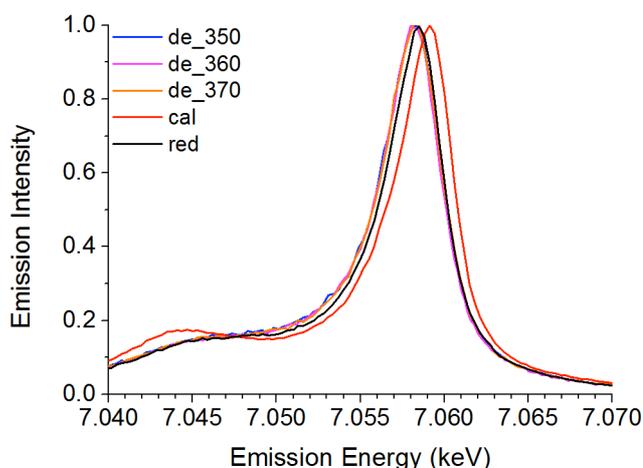


Figure 1. Fe K-Beta mainline data for the ammonia decomposition catalysts at different stages. Red (calcined sample), black (reduced sample), blue (spent sample from a reaction run at 350C), pink (spent sample from a reaction run at 360C), and orange (spent sample from a reaction run at 370 C).

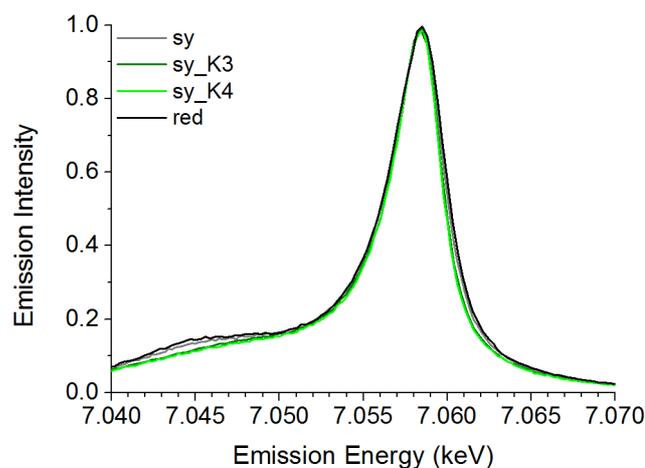


Figure 2. Fe K-Beta mainline data for the ammonia synthesis catalysts at different stages. Gray (spent sample), olive (spent sample of catalyst impregnated with KNO_3 : impregnated, calcined, reduced), green (spent sample of catalyst impregnated with KNO_3 : calcined, impregnated, calcined, reduced) and black (reduced sample).

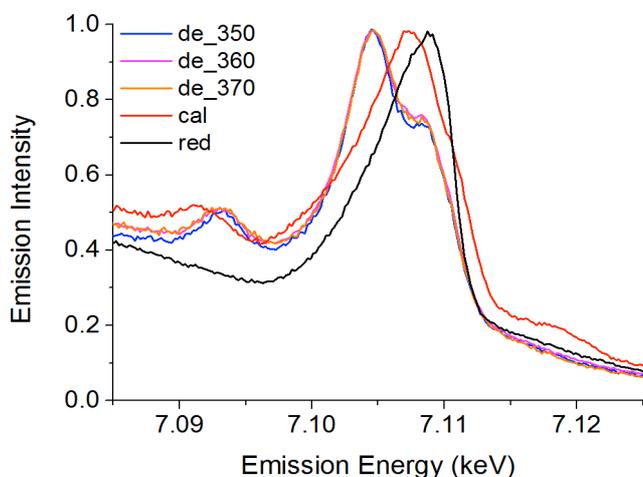


Figure 3. VtC XES data for the ammonia decomposition catalysts at different stages. Red (calcined sample), black (reduced sample), blue (spent sample from a reaction run at 350C), pink (spent sample from a reaction run at 360C), and orange (spent sample from a reaction run at 370 C).

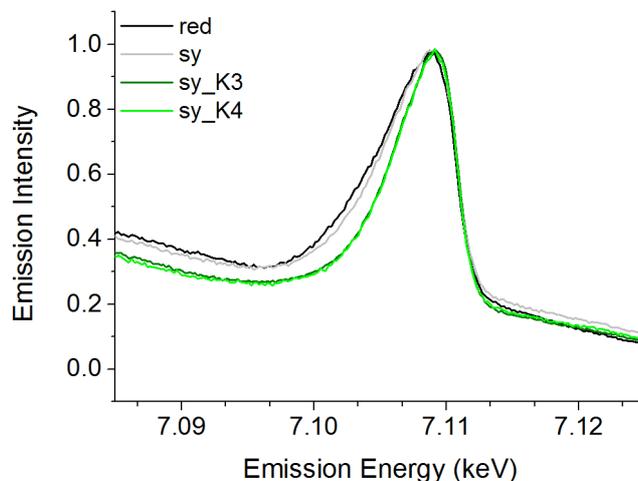


Figure 4. VtC XES data for the ammonia synthesis catalysts at different stages. Gray (spent sample), olive (spent sample of catalyst impregnated with KNO_3 : impregnated, calcined, reduced), green (spent sample of catalyst impregnated with KNO_3 : calcined, impregnated, calcined, reduced) and black (reduced sample).

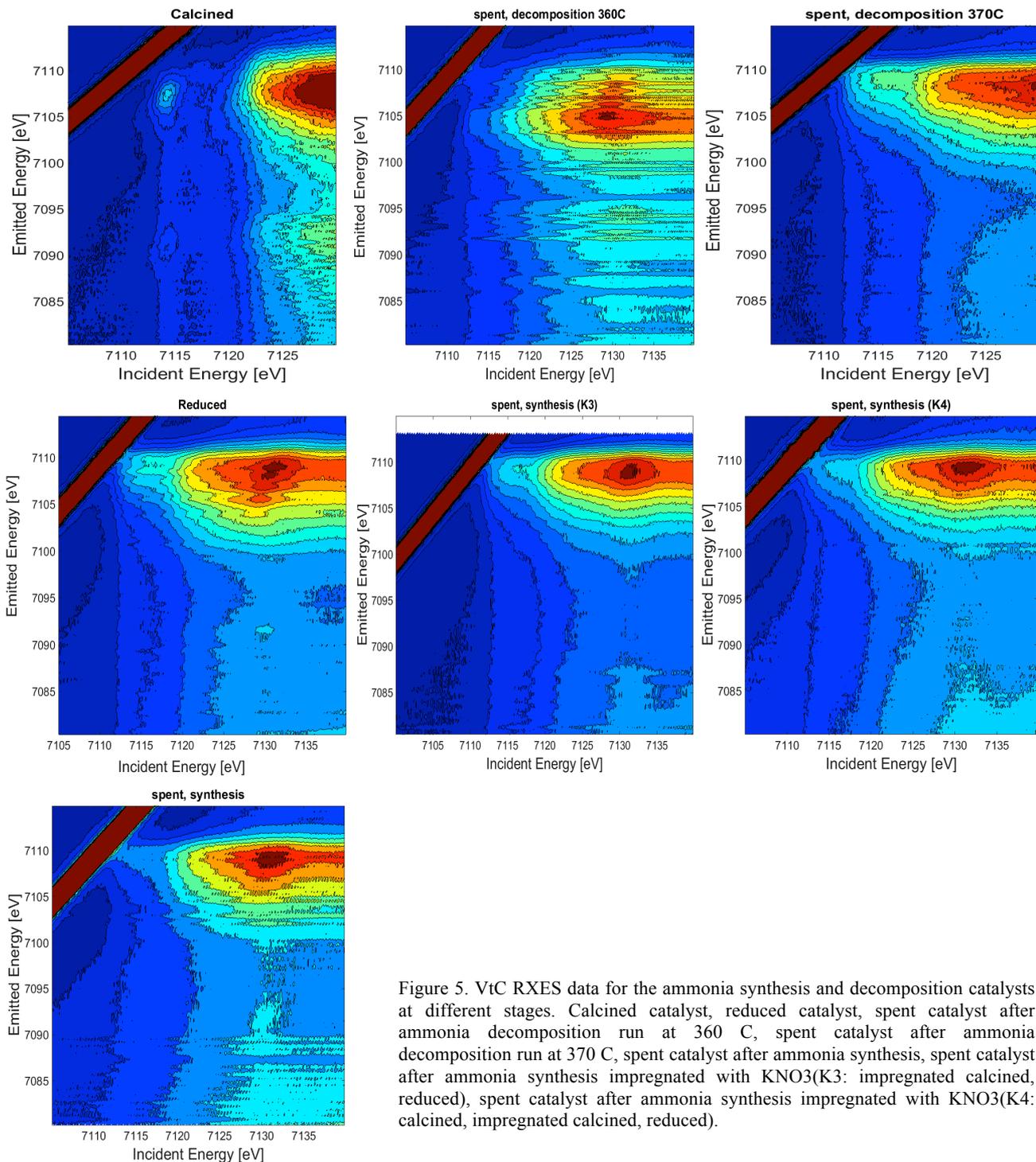


Figure 5. VtC RXES data for the ammonia synthesis and decomposition catalysts at different stages. Calcined catalyst, reduced catalyst, spent catalyst after ammonia decomposition run at 360 C, spent catalyst after ammonia decomposition run at 370 C, spent catalyst after ammonia synthesis, spent catalyst after ammonia synthesis impregnated with KNO_3 (K3: impregnated calcined, reduced), spent catalyst after ammonia synthesis impregnated with KNO_3 (K4: calcined, impregnated calcined, reduced).

The changes that occur during catalysis are more clearly seen in the VtC XES spectra shown in Figures 3 and 4 below. Of particular interest is the KB'' region of the spectra presented in Figure 3 - these data show the presence of Fe-O interaction in the calcined sample, which are no longer present upon reduction. The spent ammonia decomposition catalysts clearly show the presence of Fe-N(nitride) formation, as evidence by the increase in energy of the KB'' feature. This is consistent with bulk nitridation in the spent ammonia decomposition catalyst. Comparison of the spectra presented in Figure 4 shows that $\text{K}\beta_{2,5}$ peak is much narrower for catalyst impregnated with KNO_3 compared to the reduced catalyst or to the spent catalyst in the absence of potassium. Encouraged by the changes in the VtC XES spectra, we then obtained RIXS spectra in the VtC region. These data are shown in Figure 5 below, and clearly demonstrate a clear difference between the catalysts at different stages of the ammonia decomposition and synthesis reactions. In this context, it is also useful to take cuts of the RIXS planes in order to better highlight the changes that occur.

Figures 6 and 7 show HERFD cuts taken in the KB_{2,5} region and KB'' region of the VtC RXES spectra. As the KB_{2,5} and KB'' region corresponds to transitions from the ligand 2p and 2s, respectively, to the metal 1s core, these XAS cuts effectively correspond to "ligand selective" XAS. Here one notes that the calcined sample (shown in red) clearly correspond to oxygen bound to a oxidized form of iron. In contrast, the spent

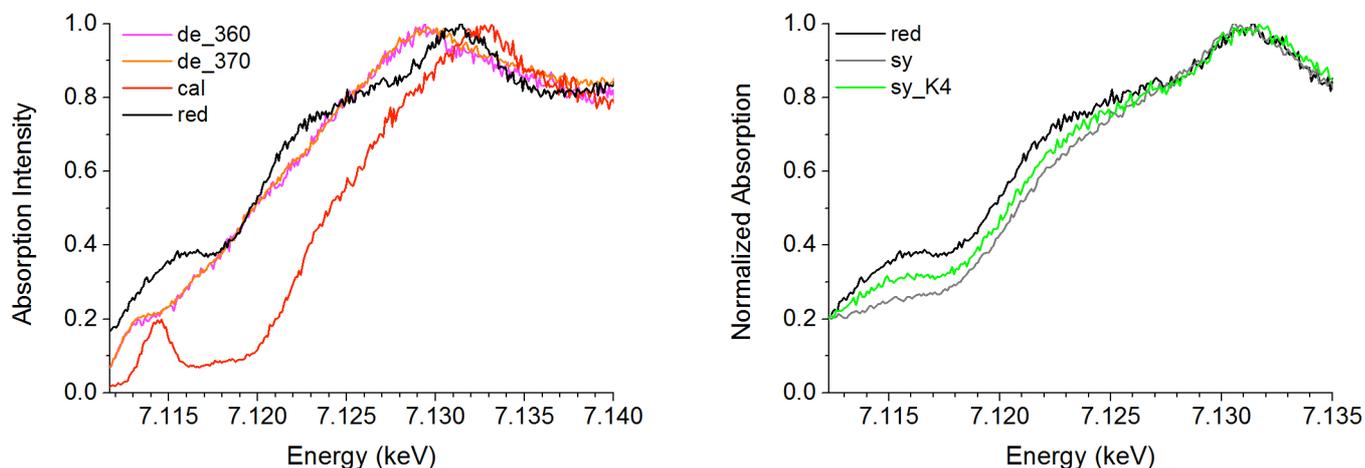


Figure 6. Cuts of the VtC RXES data for the ammonia decomposition (left) and synthesis (right) catalysts at different stages. Cuts were taken in the KB_{2,5} region.

catalysts after ammonia decomposition show a rising edge that is intermediate between the calcined and reduced catalysts. A similar trend is observed for the KB'' cuts (shown in Figure 7). Note, that the KB'' cuts for the reduced catalyst are not shown, as there is no experimentally observable intensity for the reduced catalyst in this spectral region. Nonetheless the comparison of the KB'' HERFD spectra of the spent ammonia decomposition catalyst to the calcined catalyst, suggest that the formed iron nitride species interacts with a more reduced form of Fe. From a chemical perspective this is a very interesting finding, as in principle high d-counts should not form a net bonding interaction with a nitride. This may potentially be accounted for if the nitride interacts with multiple iron sites weakly.

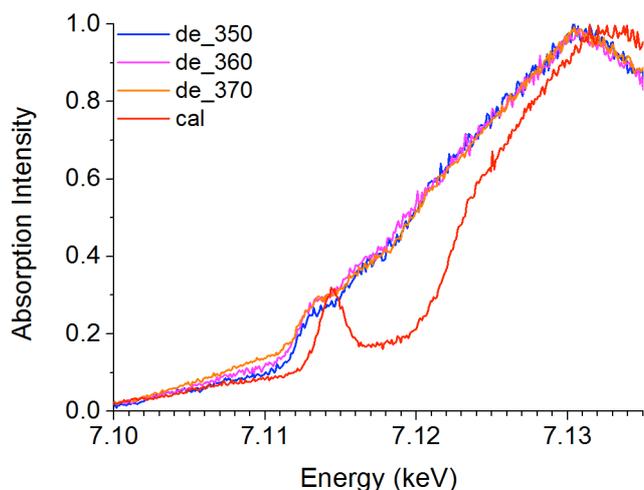


Figure 7. Cuts of the VtC RXES data for the ammonia decomposition catalysts at different stages. Cuts were taken in the KB'' region.

We are presently pursuing calculations of the Fe surface in order to reconcile the experimental results with simple inorganic bonding pictures. Calculations of the VtC RXES planes within an ROCIS approach developed in the ORCA code are also in progress. In addition, to more directly interrogate the nature of the

nitride interaction with the Fe, we have submitted a proposal to use X-ray Raman to explore the N K-edge (and also Fe L-edge). The pre-edge of the N K-edge should allow for us to directly assess the oxidation state of the interacting Fe. These studies will be applied to the ammonia decomposition catalyst investigated here, as well as ammonia synthesis catalysts.