Thermal decomposition of $(NH_4)_2[PdCl_6]$ studied by *in situ* X-ray absorption spectroscopy

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In situ X-ray absorption near edge structure (XANES) investigations were carried out at chlorine *K* edge and palladium L_3 edge to study the mechanism of the thermal decomposition of ammonium hexachloropalladate. The spectra show a characteristic feature for the initial step that might be explained as the formation of the precursor via ligand exchange ($Cl \rightarrow NH_3$). Multiple scattering calculations (Feff 8) for the Cl *K*, Pd and Rh L_3 edges were successful in simulating the XANES spectra of the precursor as well as the reference compounds $(NH_4)_2[PdCl_4]$ and $(NH_4)_3[RhCl_6]$.

Keywords: ammonium hexachloropalladate; decomposition; reaction intermediate; XANES; Feff8.

1. Introduction

The thermal decomposition of ammonium hexachlorometallates of noble metals ($(NH_4)_x[MCl_6]$) has been investigated by various techniques including thermal analysis (DTA/TG) and temperature dependent X-ray diffraction (XRD). Simultaneous mass spectrometry of the evolved gas led for M=Pd to the proposed mechanism:

$$(NH_4)_2[PdCl_6] \rightarrow \text{"}(NH_4)_2[PdCl_4]\text{"} + Cl_2 \approx 250°C \qquad (1)$$

Pd^{4+} is not stable at elevated temperatures and is reduced to Pd^{2+} in an internal redox-reaction. The proposed intermediate undergoes further reactions to form metallic Pd above 310°C according to the formal redox-reaction:

$$3(NH_4)_2[PdCl_4] \rightarrow 3Pd + N_2 + 8HCl + 4NH_4Cl \qquad (2)$$

First indications of a more complex reaction mechanism, probably including intermediates such as $Pd(NH_3)_2Cl_2$ ($T_{decomp} \approx 290°C$) and ligand exchange reactions correlated with evolved gases (e. g. HCl) were obtained in more extensive studies (Möller *et al.* 1994). As shown in a previous time-resolved X-ray absorption study (Rumpf *et al.* 1999), XANES is a promising tool to detect new ligand exchange pathways in inorganic solids. A more fundamental understanding of the internal redox-reaction in the ammonium hexachlorometallates seems to be possible and is subject of this investigation.

2. Experimental

XANES spectra have been recorded at the Center for Advanced Microstructures and Devices (CAMD, Scott *et al.* 1992) and at the Bonn electron storage ring (ELSA, Althoff *et al.* 1990). Lemonnier-type double crystal monochromators (DCM) at beamlines $5B_1$ (CAMD) and BN3 (ELSA) have been used (Lemmonier *et al.* 1978), equipped with InSb⟨111⟩ crystals for the Pd and Rh L_3 edges, as well as Si⟨111⟩ crystals for the Cl *K* edge. Transmission spectra were recorded using ionisation chambers placed in front of and behind the sample. Data analysis was performed by subtracting a linear background. For normalisation, the difference between the baseline and the absorption approx. 20 eV behind the first maximum was used. The spectra were calibrated relative to the Fermi energies of $(NH_4)_2[PdCl_6]$ and $(NH_4)_3[RhCl_6]$ which were determined by Feff 8 calculations (cp. section 3.2)

Sample preparation was carried out by spreading ammonium hexachlorometallate on the surface of thin filter plates consisting mainly of SiO_2 which are adapted to the dimension of the *in situ* reaction cell. A constant helium flow was chosen as reaction atmosphere to eliminate evolving chlorine gas and to reduce the absorption of the gas atmosphere in the beam pathway. In our measurements, a typical heating rate was 1.5 K/min in order to achieve a moderate temperature rise of 15 to 20 K during the recording time of 10 and 14 minutes per spectrum.

Reference samples were obtained from Aldrich Chemicals (Pd, solid NH_4Cl), as well as synthesized starting from simple precursors obtained from Merck Chemicals (instructions published in Brauer 1981).

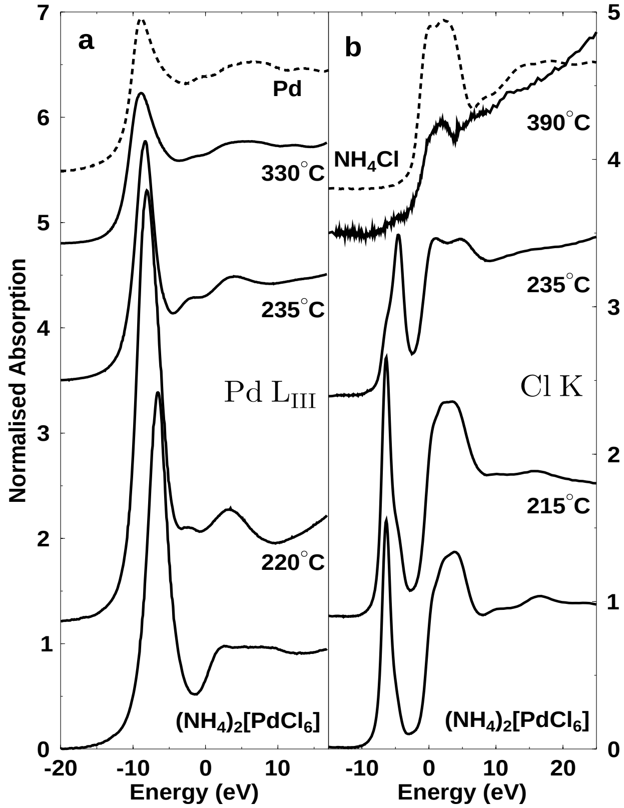

Figure 1
Cl *K* and Pd L_3 XANES spectra of the reaction $(NH_4)_2[PdCl_6] \rightarrow Pd$.

3. Results

3.1. In situ XANES investigation of $(NH_4)_2[PdCl_6] \rightarrow Pd$

Cl K and Pd L_3 XANES spectra of the *in situ* reaction $(NH_4)_2[PdCl_6] \rightarrow Pd$ are shown in Fig. 1. The final product Pd and small amounts of NH_4Cl can be identified by comparison with XANES reference spectra of Pd powder and solid NH_4Cl (dashed lines in Fig. 1). Furthermore, it was possible to identify two intermediates which occur at the medium temperature of the heating intervall at 220° C respectively 235° C and reveal significant differences in form and position of the shape resonances. The identification was supported by analysing the time-resolved series in two different manners as shown in Fig. 2. Voigt profiles have been fitted to the pre-edge peak (Cl K edge) as well as to the white line of the Pd L_3 edge to analyse the position of the maximum. This method is not only a quick tool to visualize differences in a series of spectra but it is also useful to determine the valence state. The integration method by Capehart (Capehart *et al.* 1995) gives similar results.

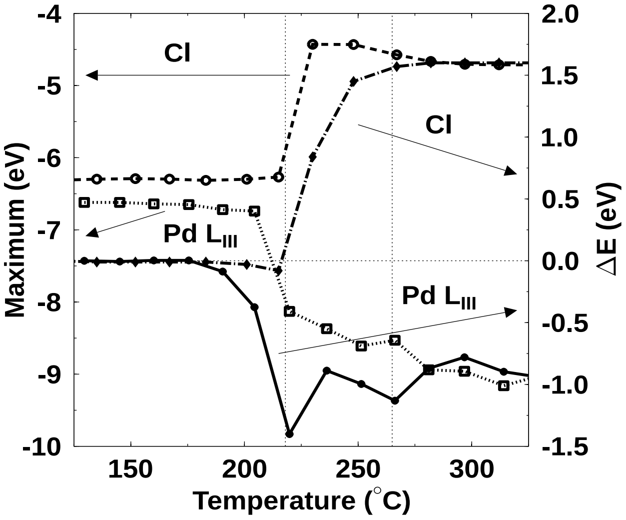

Figure 2
Position of pre-edge peak and white line of the spectra shown in Fig. 1 (y1 axis) as well as the energy shift relative to the $(NH_4)_2[PdCl_6]$ spectrum (ΔE) determined by integration of the edge region (y2 axis).

Regarding the Pd L_3 edge, it is possible to interpret the energy shift in Fig. 2 by a decreasing valence starting from the initial state of Pd^{4+}. The first intermediate is formed at about 220° C (Pd^{2+}) whereas a second product can be observed in the following spectrum at 235° C (Pd^{2+}). Starting at 300° C, the formation of metallic Pd can be observed which is the dominant contribution to the XANES spectra at 330° C as shown in Fig. 1a.

The results obtained at the Cl K edge correspond very well to these findings. The two intermediates are shown in Figure 1b. A shoulder in the pre-edge peak of the 235° C spectrum is the contribution of some remnants of the first intermediate. The observation of both states in the same spectrum is possible due to a slight temperature gradient on the sample as well as the involved diffusion process which yields a small reaction velocity.

At above 350° C, the chlorine spectra have a very small signal-to-noise ratio since evolved Cl_2 and HCl gas molecules are carried away by the constant helium flow passing through the reaction cell. Nevertheless, regarding the 390° C spectrum in Fig. 1, the formation of NH_4Cl can be observed (cf. reference compound of solid NH_4Cl in this Figure). The spectrum does not give evidence of a characteristic pre-edge peak since the Cl^- anion has a completely filled valence shell omitting the $1s \rightarrow 4p$ electron transition. Therefore, it can be excluded that chlorine is still bound to Pd at this temperature.

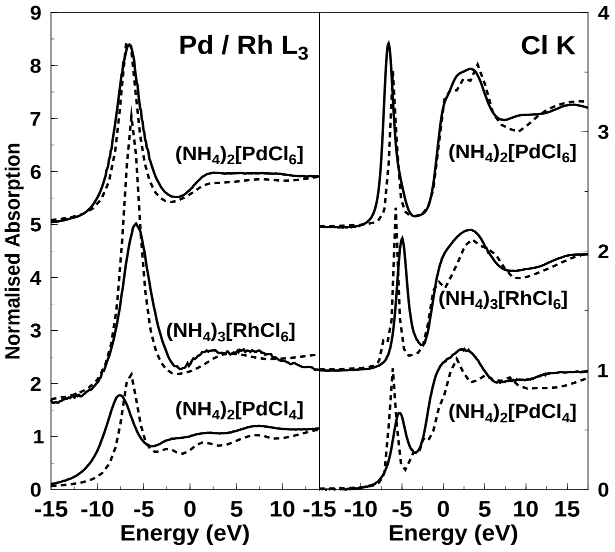

Figure 3
Multiple scattering Feff 8 simulations (dashed lines) compared to the reference compounds (solid lines).

3.2. Feff 8 multiple scattering calculation of ammonium chlorometallates

The latest version of the Feff multiple scattering programm (Feff 8: Ankudinov *et al.* 1998) shows an improved capability in simulating XANES features of a broad number of elements. Goal of this study was to identify the mechanism of the $(NH_4)_2[PdCl_6]$ thermal decomposition. Therefore, a variety of reference compounds have been measured and we tried to reproduce the spectral features using Feff 8. The most successful results are shown in Fig. 3 which comprise the Rh L_3, Pd L_3 and Cl K XANES spectra of $(NH_4)_3[RhCl_6]$, $(NH_4)_2[PdCl_6]$ and $(NH_4)_2[PdCl_4]$.

For the simulation, the self-consistent field option of the program was chosen to calculate the scattering muffin-tin potential. Up to fifteen iteration steps were carried out on a radius of about 30 neighbouring atoms. Full multiple scattering was applied on a cluster of 87 atoms using the XANES option of the program.

The simulation was restricted to a relatively small cluster size because of the limited calculation time meaning that $(NH_4)^+$ was simply modelled as nitrogen backscatterers without considering the hydrogen contribution. This fact might explain small differences between simulation and experimental data. In addition, Feff8 gives less accurate results when the O_h symmetry around the central atom (Pd) is broken (Ankudinov 2000). However, the quality of the fits speaks for itself and the similarity between the measured and the calculated Pd L_3 shape resonances is particularly astonishing.

4. Discussion

It has been supposed for some time that the thermal decomposition of ammonium hexachloropalladate starts with a ligand exchange corresponding to $MCl_6 \rightarrow M(NH_3)Cl_5$. This reaction scheme is based on a study concerning the decomposition of $(NH_4)_3[RhCl_6]$, which has been investigated by XRD, infra-red spectroscopy (IR) and preparative techniques yielding to the identification of $(NH_4)_2[Rh(NH_3)Cl_5]$ as intermediate (Meyer and Möller 1991).

So far, it has been impossible to observe a similar intermediate for $(NH_4)_2[PdCl_6]$ and no indications for a ligand exchange were found by all applied standard methods.

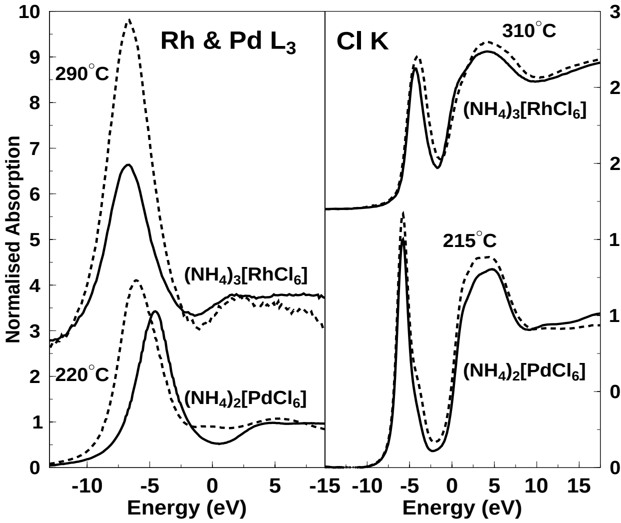

Figure 4

Ligand exchange (Cl → NH_3) in the thermal decomposition of $(NH_4)_2[PdCl_6]$) and $(NH_4)_3[RhCl_6]$ (solid lines) which occurs at about 220°C (Pd) and 300°C (Rh), respectively (dashed lines)

In Fig. 4, Cl *K* and M L_3 XANES spectra, however, suggest that $(NH_4)_3[RhCl_6]$ and $(NH_4)_2[PdCl_6]$ follow the same mechanism. The ligand exchange process in the rhodium sample is coupled with an increasing white line intensity (Rh L_3 edge) and the same effect can be observed at the Pd L_3 edge in Fig. 4a. In addition, an edge shift resulting from the change of valence from IV → II can be observed whereas rhodium keeps its valence (III). Furthermore, the chlorine *K* edge of both compounds (Fig. 4b) reveals the same characteristic changes during the ligand exchange, namely an increasing intensity of the main resonance when passing the formation temperature of the first intermediate (215°C/310°C) and a decreasing and less pronounced shoulder peak (approx. at 0 eV). The result implies that the first reaction step is the formation of an ammine complex via ligand exchange to enable the internal redox-reaction between the metal cation and the NH_3 ligand. This is the characteristic step in the thermal decomposition. Unfortunately, Feff8 simulations taken on ligand exchanged $Rh(NH_3)Cl_5$ respectively $Pd(NH_3)Cl_5$ model systems were not very convincing since the code is less successful when the perfect O_h symmetry is broken. As a matter of fact, an electron donating NH_3 ligand is expected to result in an increased white line but since the local symmetry is changed the problem is more complex. Using the Feff 8 code, we were not yet able to find any electronical or geomtrical configuration resulting in an increased white line intensity. Further improvements of the FEFF code would be useful and further experiments might also be necessary to obtain a final answer.

The identification of the second intermediate is more complex. A variety of compounds seems to be involved and the decomposition is strongly influenced by reaction conditions like gas flow and temperature ramp. Since it is possible to stop the reaction after the formation of the second intermediate and to even obtain a stable crystalline compound, there are more efficient tools to analyse this product than *in situ* XANES, particularly on ground of the evolved chlorine gas which influences the quality of the spectra.

IR and XRD spectra revealed that this second intermediate consists of a mixture of at least trans-$Pd(NH_3)_2Cl_2$ and $(NH_4)_2[PdCl_4]$, but linear combination of the two XANES reference spectra did not result in a satisfying fit. It is a further hint, that additional compounds are involved in the reaction mechanism.

A more detailed picture may be possible taking XANES spectra with a significantly higher time-resolution. This can be achieved using the energy dispersive monochromator located at beamline BN1 of ELSA (cf. Rumpf *et al.* 1999) and it is certainly the next step in the course of our investigations.

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