

Experiment Report Form



Experiment title: Solid-state thermal decomposition of platinum group metals coordination compounds: *in situ* time- and temperature-resolved PXRD study

Experiment number:
CH-5164

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We investigated a thermal decomposition of over 20 coordination compounds in Ar (inert atmosphere) and H₂/Ar flow (reductive atmosphere). Individual compounds (NH₄)₂[Ir/Pd/Re/Os/PtCl₆], (NH₄)₂[IrBr₆], (NH₄)₃[Ir/RhCl₆], [Pd/Pt(NH₃)₄][Os/ReCl₆], (NH₄)₂[Os_xPt_{1-x}Cl₆], [RuNO(NH₃)₄OH][Cu(C₂O₄)₂(H₂O)_{1.5}], [RuNO(NH₃)₅]₂[Cu(C₂O₄)₂(H₂O)₂][Cu(C₂O₄)₂H₂O]₂·2H₂O, [Ir(NH₃)₅Cl][OsCl₆], xH₂[PtCl₆]@graphene, were chosen to support our systematic study of the thermal decomposition of coordination compounds. Compounds were used as single-source precursors for nanoporous refractory alloys active as heterogeneous and electrocatalysts. Thermal decomposition was performed in dynamic gas-flow with constant heating ramp (6 or 12 K/min); powder diffraction data were collected with time-resolution (scans were collected every 2 seconds); simultaneously, evolved gases were analysed using mass-spectrometry. Data obtained will be further supported by complementary techniques such as in-house TG–DSC–EGA curves, SEM/EDX, SEM, as well as IR and Raman *in situ* and *ex situ* studies; to characterise chemical nature of key intermediates we are also going to perform *in situ* quick-EXAFS studies (ROCK / SOLEIL / March 2018 and BM23 / ESRF / April-May 2018). Typical temperature-dependent PXRD patterns for [Pd/Pt(NH₃)₄][Os/ReCl₆] are given in **Figure** below. Their thermal decomposition in Ar and H₂/Ar can be associated with a formation of (NH₄)₂[Os/ReCl₆] + Pt/Pd. Further heating results in a formation of *fcc*-structured defect single-phase alloy which decomposes with heating to thermodynamically stable *fcc+hcp* mixture.

Thermal decomposition of $(\text{NH}_4)_2[\text{Os}_{0.40}\text{Pt}_{0.60}\text{Cl}_6]$ has been investigated to support our study of Os—Pt alloys under high-pressure high-temperature conditions. $(\text{NH}_4)_2[\text{Os}_x\text{Pt}_{1-x}\text{Cl}_6]$ salts were used as single-source precursor for electrocatalytically active Os—Pt alloys as well as were applied to probe Os—Pt phase diagram under high-pressure. In Ar flow, $(\text{NH}_4)_2[\text{Os}_{0.40}\text{Pt}_{0.60}\text{Cl}_6]$ gives directly *fcc*- $\text{Os}_{0.40}\text{Pt}_{0.60}$ (Figure below). In H_2 flow, $(\text{NH}_4)_2[\text{Os}_{0.40}\text{Pt}_{0.60}\text{Cl}_6]$ transforms to β -*trans*- $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2] + \text{NH}_4\text{Cl} + \text{fcc-Os}_{0.40}\text{Pt}_{0.60}$ (above 200 °C) and later to α -*trans*- $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2] + \text{fcc-Os}_{0.40}\text{Pt}_{0.60}$ (above 250 °C). Above 300 °C, only *fcc-Os}_{0.40}\text{Pt}_{0.60} can be detected. Further annealing results in a formation of *fcc+hcp* mixture. $[\text{Ir}(\text{NH}_3)_5\text{Cl}][\text{OsCl}_6]$ shows similar behaviour: direct formation of two phase $\text{Os}_{0.50}\text{Ir}_{0.50}$ in Ar and formation of $(\text{NH}_4)_2[\text{OsCl}_6] + \text{Ir}$ with further crystallisation of single phase *fcc-Os}_{0.50}\text{Ir}_{0.50}. We also investigated thermal decomposition of $(\text{NH}_4)_2[\text{Ir}/\text{PdCl}_6]$, $(\text{NH}_4)_2[\text{IrBr}_6]$, and $(\text{NH}_4)_3[\text{Ir}/\text{RhCl}_6]$. It is surprising that all salts decompose with a formation of crystalline intermediate compounds such as $(\text{NH}_4)_2[\text{PdCl}_4]$ and $(\text{NH}_4)_2[\text{Ir}/\text{RhCl}/\text{Br}_5(\text{NH}_3)]$. Such findings will support our previous studies where Ir-based compound (**now detected as $(\text{NH}_4)_2[\text{IrCl}_5(\text{NH}_3)]$**) was proposed as key intermediate in a formation of Os—Ir and Re—Ir nanoporous metastable alloys.**

It seems that we can now formulate very general trend in the thermal decomposition of many coordination compounds. In inert atmosphere, compounds are stable up to relatively high temperatures and form metallic products directly without formation of visible crystalline intermediates. In reductive atmosphere, *fcc*-structured metallic products can be found at relatively low temperatures with a mixture of $(\text{NH}_4)_2[\text{MCl}_6]$ as the main crystalline intermediate. Further heating results in a formation of *fcc*-structured alloys which decompose to *fcc+hcp* mixtures at high temperature according to equilibrium metallic phase diagrams. Early studies of thermal behaviour of coordination compounds were based on sporadic TG–DSC and *ex situ* PXRD (mainly in house), IR and Raman data. Previously in the literature, opposite trends were proposed: sequential formation of several intermediates in inert atmosphere and absence of any crystalline structurally characterizable intermediates in reductive environment. Likely, some intermediates were previously interpreted wrongly as products of degradation of labile and reactive species.

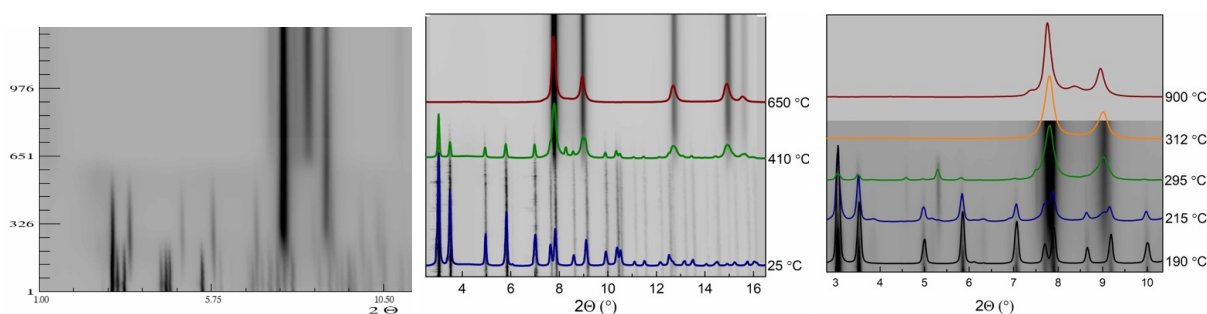


Figure Thermal decomposition of $[\text{Pt}(\text{NH}_3)_4][\text{OsCl}_6]$ in 2 vol.% H_2/Ar (*left*), $(\text{NH}_4)_2[\text{Os}_{0.40}\text{Pt}_{0.60}\text{Cl}_6]$ in Ar (*middle*) and 2 vol.% H_2/Ar flow (*right*).

We are going to publish our data very soon in the following research papers: Martynova, Yusenko *et al.* (2018): Ruthenium-rich Cu—Ru alloys from single-source precursors. *New J. Chem.*, *in preparation*; Asanova, Yusenko *et al.* (2018): Key intermediates in thermal decomposition of iridium chloride, bromide and fluoride coordination compounds. *Inorg. Chem.*, *in preparation*; Asanova, Yusenko *et al.* (2018): Thermal decomposition of $[\text{M}^{\text{I}}(\text{NH}_3)_4][\text{M}^{\text{II}}\text{Cl}_6]$ ($\text{M}^{\text{I}} = \text{Pt}, \text{Pd}$; $\text{M}^{\text{II}} = \text{Os}, \text{Re}$). *PCCP*, *in preparation*.