EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

Experiment Report Form

	Experiment title: Study of formation of multicomponent nanoporous refractory alloys from single-source precursors using in situ time- and temperature-resolved PDF	**Experiment number**: CH-5511
Beamline: ID22	**Date of experiment**: from:02.11.2018 to:05.11.2018	**Date of report**: 12.08.2019
Shifts: 12	**Local contact(s)**: Dr. Catherine Dejoie	*Received at ESRF:*

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Report:

In the frame of our experiemnt, we collected in situ diffractino data upon heating of a number of industrially important precursors for refractory alloys. Thermal decomposition of $(NH_4)_2[PtCl_6]$, $(NH_4)_2[PtBr_6]$, $(NH_4)_2[PtI_6]$, $[Ir(NH_3)_5Cl][OsCl_6]$, $[Co(NH_3)_6][Fe(C_2O_4)_3]\cdot 3H_2O$ was investigated in inert (He) and reductive (5 % H_2 in He) flows. Key intermediates were isolated and characterised structurally.

As an example, thermal decomposition of $[Co(NH_3)_6][Fe(C_2O_4)_3]\cdot 3H_2O$ in reductive atmosphere results in a formation of catalytically active nanostructural powder (5 vol.%-H_2 in He, Figure below). At the first stage, $[Co(NH_3)_6][Fe(C_2O_4)_3]\cdot 3H_2O$ forms crystalline anhydrous $[Co(NH_3)_6][Fe(C_2O_4)_3]$ and further amorphous intermediate $[M(C_2O_4)(NH_3)_2]$ with a PDF curve similar to *cis*-$[Cu(C_2O_4)(H_2O)_2]_n$, *Pccm*. Such intermediate has no long order above r = 8–9 Å. Further exothermic reaction might correspond to a formation of crystalline phase similar to *trans*-$[Fe(C_2O_4)(NH_3)_2]_n$. Upon further heating, *fcc*-$Fe_{0.5}Co_{0.5}$ alloy can be isolated.

Thermal decomposition of other compounds also occures without formation of crystalline intermediates, nevertheless, their structural characteristics can be obtained from analysis of PDF curves.

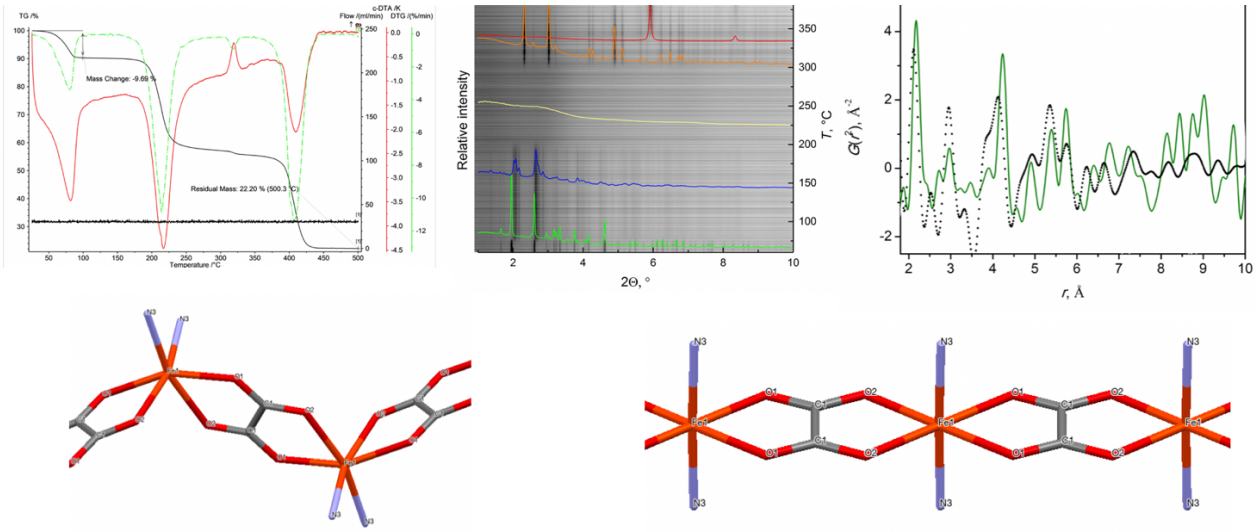

Figure TG/DTG/DTA curves for $[Co(NH_3)_6][Fe(C_2O_4)_3]\cdot 3H_2O$ in 5 vol.%-H_2 in He (10 K/min, *left*), temperature dependent *in situ* PXRD curves upon heating in 5 vol.%-H_2 in He (10 K/min, λ = 0.2065773 Å, middle), pair distribution functions for amorphous intermediate (225 °C, dots) with modelled curve corresponding to *cis*-$[M(C_2O_4)(NH_3)_2]_n$ (left structure). *Cis*-polymeric chain might transfer further to *trans*-chain (right structure).