



JOURNAL OF
SYNCHROTRON
RADIATION

Volume 30 (2023)

Supporting information for article:

CatMass – Software for calculating optimal sample masses for X-ray absorption spectroscopy experiments involving complex sample compositions

Jorge E. Perez-Aguilar, Ash Caine, Simon R. Bare and Adam S. Hoffman

S1. Sample Building Examples

The figure displays three instances of the 'Sample Builder' software interface. Each window has a title bar 'Sample Builder' and a close button. The interface is divided into two main sections: 'Supported Metal Complexes' and 'Supported Metal Complexes'. The left window shows a configuration for 1 wt% Pt on Al₂O₃. The middle window shows a configuration for 1 wt% Ir(CO)₂ on MgO. The right window shows a configuration for 5 wt% Pt₃Sn on Al₂O₃. Each window includes input fields for 'Support', 'Metal Site #1', 'Metal Site #1 Loading', 'Metal Site #2', and 'Metal Site #2 Loading'. There are also 'Reset' and 'Update Sample' buttons, and a 'Diagnostic' field at the bottom. Notes are provided for each configuration: 'Note: wt% must reflect the entire metal site.' and 'Note: Metal Site 2 is an optional field.' for the left and right windows, and 'Note: for metal oxides or organometallic complexes' and 'Note: only define complex loading OR metal loading' for the middle window.

Figure S1 Examples of several complex catalysts when using the “Sample Builder” window; Left: 1 wt% Pt on Al₂O₃ (Aitbekova *et al.*, 2022); Middle: 1 wt% Ir(CO)₂ on MgO where the wt% is percent metal (Hoffman *et al.*, 2018); Right: 5 wt% Pt₃Sn nanoparticles on Al₂O₃ (Baraa Werghi *et al.*, 2023). Clicking “Update Sample” will convert these inputs into a stoichiometric composition and pass the values to the main window.

S2. Ytterbium oxide (Yb₂O₃) details

S2.1. Experimental methods

Extended X-ray absorption fine structure (EXAFS) measurements were conducted at beamline 10-2 at the Stanford Synchrotron Radiation Lightsource (SSRL). Beamline 10-2 has a 33-pole, 1.72-Tesla wiggler source and a double-crystal, liquid-nitrogen-cooled Si(111) monochromator. Step-scan spectra were collected in transmission mode with nitrogen-filled ion chambers. A Cu foil was scanned simultaneously with the sample for energy calibration.

S2.2. Choosing a reference foil for the measurement

When measuring a material that a reference foil would be difficult to obtain, e.g. Yb₂O₃, *CatMass* can be used to visualize where standard metal foils would appear in *k*-space for reference foil selection. Using the “Sample and Dilution Definition” panel, potential elements to be used as a reference can be input as “dilutents”. When the plot option is selected when calculating the results, the edges of the potential references are displayed in the *k*-space plot. In the example presented in Fig. S2, when scanning the Yb L_{III}-edge either the Cu or Zn reference foils could be used as a reference for internal energy calibration.

S3. Example calculation of alternative solutions when using CatMass

S3.1. Smear on tape

CatMass - XAS Sample Mass Calculator

File View

Sample and Dilution Definition

Sample Builder

Sample: Stoichiometry: O65.508453Ca1.000000Ce Chemical Formula

Diluent: Chemical Formula

Mass Dilution Ratio: # #

Reset Calculate Diluted Sample Chemical Formula

File Path

None

Edge Scan and Absorption Properties Definition

Diluted Sample Chemical Formula: 8Ca1.000000Ce32.254226

Element to be Scanned: Ca

Edge to be Scanned: K

XAS Cells:

Capillary Diameter [mm]: 3

Bed length [1 cm]: 1

Pellet Diameter [mm]: 7

Other

Sample Area \perp to Beam [cm²]: 0.38

Catalyst Sample Absorption at E0 + 50 eV: 2.6

Sample at 45°

Show Plot

Reset

Results

Calculate Sample Mass

Diluted Sample Mass [mg]: 2.56

Estimated Edge Step: 0.0095

Sample Mass [mg]: 2.56

Diluent Mass [mg]: 0.00

Edge Energy [eV]: 4038

X-ray transmission through media

Note: Edge step at: E0 ± 45 eV, consider fluorescence

CO-ACCESS Consortium for Operando and Advanced Catalyst Characterization via Electronic Spectroscopy and Structure

SSRL

Figure S4 Example of 1wt% CaO/CeO₂. Calculation could not be optimized with a diluent to prepare enough sample material into a 7 mm pellet. Based on the sample mass value, smearing the sample would make the most physical sense to prepare inside a glovebox.

S3.2. Stacked pellets

CatMass - XAS Sample Mass Calculator

File View

Sample and Dilution Definition

Sample Builder

Sample: Stoichiometry: g5505.401786Os1.000000 Chemical Formula

Diluent: Chemical Formula

Mass Dilution Ratio: # #

Reset Calculate Diluted Sample Chemical Formula

File Path

None

Edge Scan and Absorption Properties Definition

Diluted Sample Chemical Formula: g5505.401786Os1.000000

Element to be Scanned: Os

Edge to be Scanned: L3

XAS Cells:

Capillary Diameter [mm]: 3

Bed length [1 cm]: 1

Pellet Diameter [mm]: 7

Other

Sample Area \perp to Beam [cm²]: 0.38

Catalyst Sample Absorption at E0 + 50 eV: 1.77

Sample at 45°

Projected Sample Area to Beam [cm²]: 0.27

Projected Catalyst Sample Absorption at E0 + 50 eV: 2.50

Show Plot

Reset

Results

Calculate Sample Mass

Diluted Sample Mass [mg]: 59.81

Projected Estimated Edge Step: 0.0099

Sample Mass [mg]: 59.81

Diluent Mass [mg]: 0.00

Edge Energy [eV]: 10871

X-ray transmission through media

Note: Edge step at: E0 ± 45 eV

CO-ACCESS Consortium for Operando and Advanced Catalyst Characterization via Electronic Spectroscopy and Structure

SSRL

Figure S5 Example of 0.1wt% OsO₂/MgO. Calculation could not be optimized to satisfy the mass requirement range of one 7 mm pellet and keep a reasonable edge step for fluorescence. However, two pellets stacked on top of each other would add up to the estimated mass needed.

S3.3. Total absorption measurement

Sample and Dilution Definition

Sample Builder

Stoichiometry: e1289.593912Os1.000000 Chemical Formula

Mass Dilution Ratio: # #

Reset Calculate Diluted Sample Chemical Formula

File Path

None

Edge Scan and Absorption Properties Definition

Diluted Sample Chemical Formula: e1289.593912Os1.000000

Element to be Scanned: Os

Edge to be Scanned: L3

XAS Cells:

Capillary Diameter [mm]: 3

Pellet Diameter [mm]: 7

Other

Bed length [1 cm]: 1

Sample Area \perp to Beam [cm²]: 0.38

Catalyst Sample Absorption at E0 + 50 eV: 7

Sample at 45°

Projected Sample Area to Beam [cm²]: 0.27

Projected Catalyst Sample Absorption at E0 + 50 eV: 9.90

Show Plot

Reset

Results

Calculate Sample Mass

Diluted Sample Mass [mg]: 20.14

Projected Estimated Edge Step: 0.0406

Sample Mass [mg]: 20.14

Diluent Mass [mg]: 0.00

Edge Energy [eV]: 10871

X-ray transmission through media

Note: Edge step at: E0 ± 43 eV

SSRL

Figure S6 Example of 0.1 wt% OsO₂/CeO₂. Calculation could not be optimized to satisfy the mass requirement range of one 7 mm pellet and keep a reasonable edge step for fluorescence. Increasing the sample absorption to meet the minimum requirement of packing the sample in a 7 mm pellet would be ideal. Smear on tape could yield measurable data, however the edge step is an order magnitude smaller and would require a high number of scans. Regardless, the use of a solid-state detector would be needed for the measurement and a simultaneous off axis reference foil measurement.

References

- Aitbekova, A., Zhou, C., Stone, M. L., Lezama-Pacheco, J. S., Yang, A. C., Hoffman, A. S., Goodman, E. D., Huber, P., Stebbins, J. F., Bustillo, K. C., Ercius, P., Ciston, J., Bare, S. R., Plessow, P. N. & Cargnello, M. (2022). *Nat. Mater.* **21**, 1290–1297.
- Baraa Werghi, Amani Ebrahim, Simon Bare & Matteo Cargnello (2023). *Small*, 2207956.
- Hoffman, A. S., Debeve, L. M., Zhang, S., Perez-Aguilar, J. E., Conley, E. T., Justl, K. R., Arslan, I., Dixon, D. A. & Gates, B. C. (2018). *ACS Catal.* **8**, 3489–3498.