CAPTURING CATALYST STRAIN DYNAMICS DURING *IN SITU* CO OXIDATION

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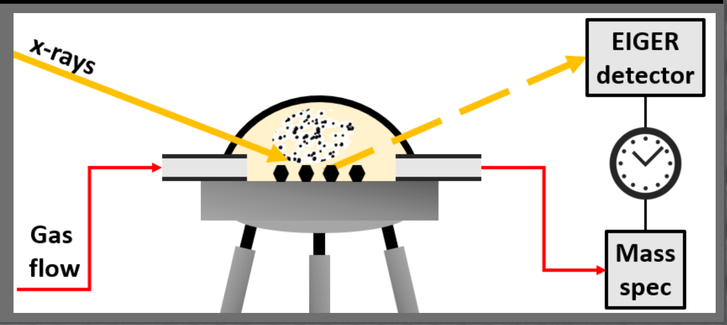
Motivation

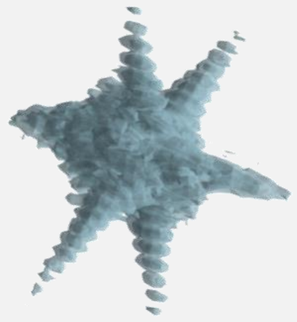
- Nanoparticle (NP) assisted chemical reactions
- site-specific adsorption and lattice strain [1]
- *In situ* Bragg Coherent Diffraction Imaging (BCDI) [2,3]
- Approach second regime without loss of resolution
- Correlate changes with the arrival of reactants
- Localised adsorption rate

In situ BCDI

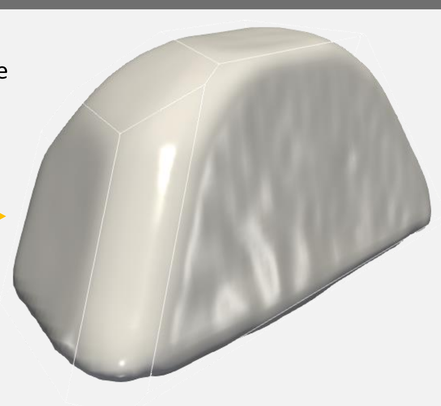
Gas panel => reactant flow
Mass spectrometer => product analysis
Rocking curve => 3D Pt **(111)**
Eiger2M => fast dynamics
pynx => phase retrieval [4]



Fast Scan BCDI: real-time evolution

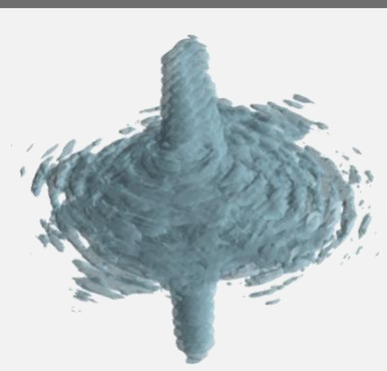


- Continuous sweep of eta angle
- Time per frame ~ 5 ms
- Total scan time <20 s

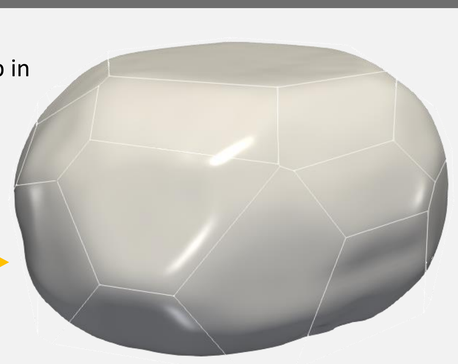


- [111] top and bottom
- Large twin boundary
- Dominated by (111) facets

Gas-triggered stroboscopic BCDI

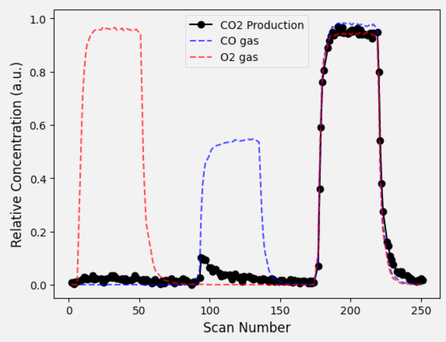


- Repeat reaction at each step in eta (120 * 0.01 deg)
- Binned to improve counts
- Effective count time = 30 s
- Time resolution = 0.25 s



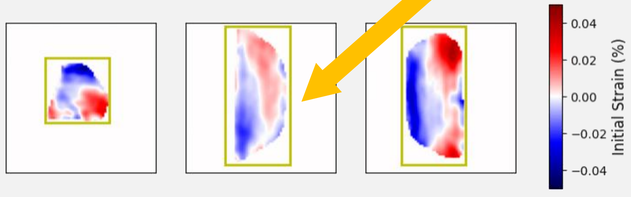
- [111] top and bottom
- Litany of facets

Reaction conditions

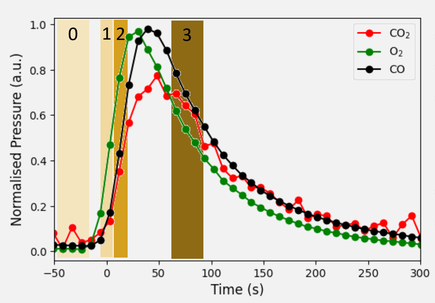


Performed under following conditions:
1. O_2 25 mbar
2. CO 25 mbar (CO_2 produced ~2 min)
3. Co:O_2 50:25 mbar (oxidation reaction)

COMPARE TO THE INITIAL CONIDITON

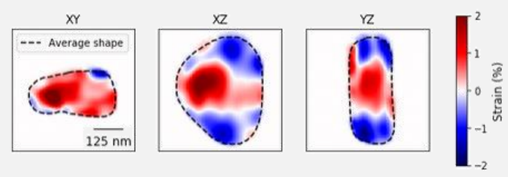


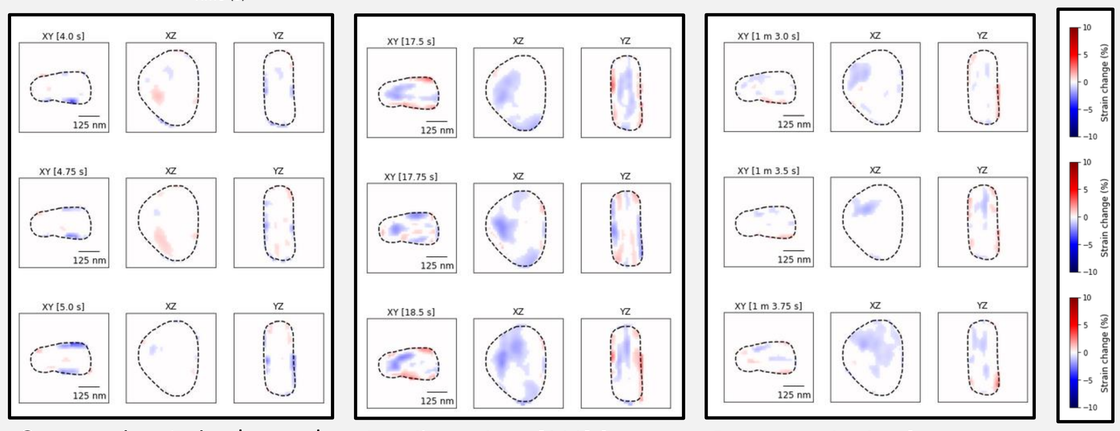
Reversible particle evolution



- O_2 precedes CO (10 s)
- Immediate oxidation
- Peak values:
  - O_2 - 7 mbar
  - CO - 30 mbar
- 6 min interval
- Recovery of initial state

COMPARE TO MEAN STRAIN BEFORE t_0





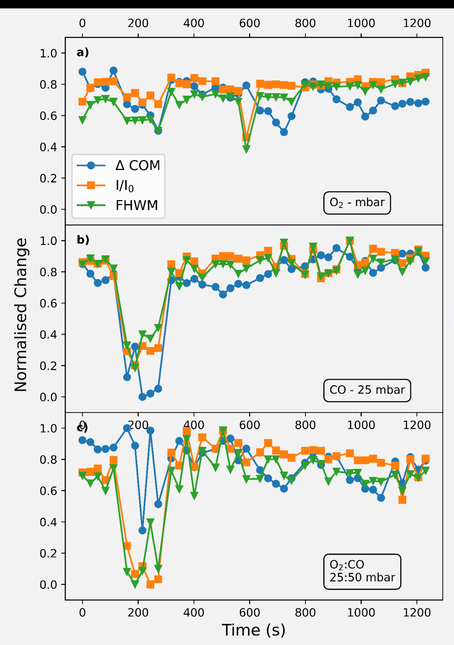
Compressive strain observed during oxygen arrival

Tensile strain at [111] facets. Widespread change

Recovery ~1 min after gas arrival. Reversibility observed

ISSUE: why compression in bulk?
Strain computed with reference to reconstructed phase. Not sensitive to isotropic evolution. Need to correct with respect to the average lattice spacing (computed from Bragg scattering angle).

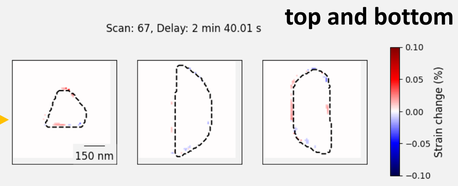
Peak evolution



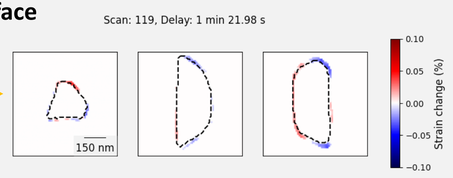
Strain evolution

- Small changes under oxygen environment
- Under CO, oxidation occurs due to adsorbed O on surface
- Changes occur <20 s

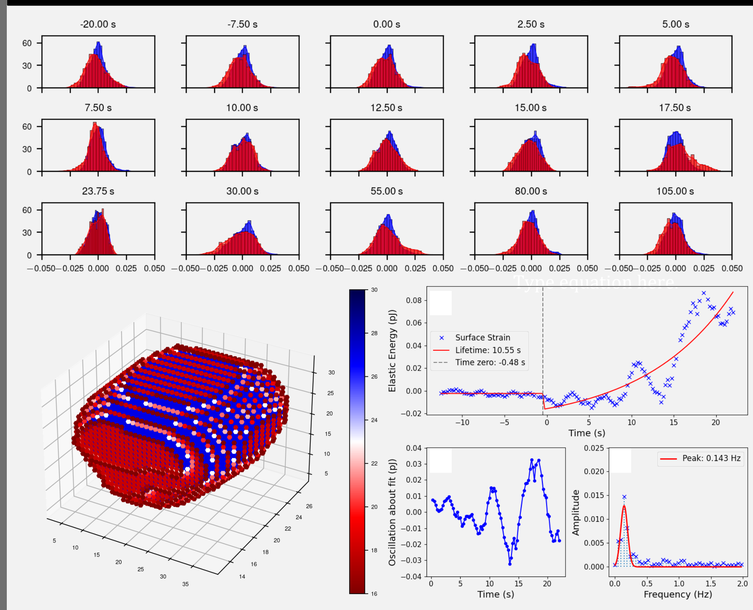
Tensile strain at top and bottom



Strain evolution at surface



Global strain (heterogenous + homogenous)

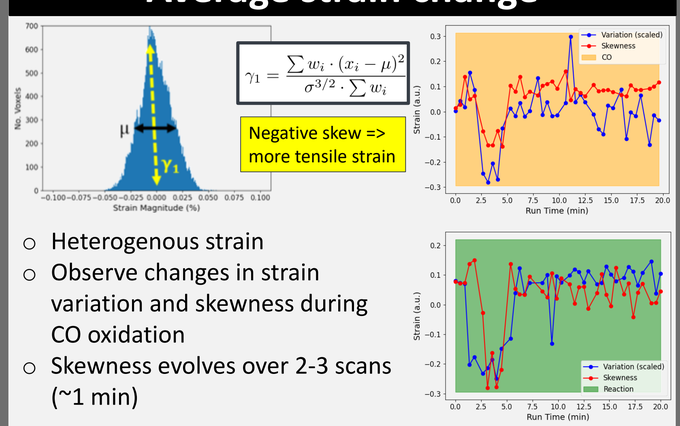


- Separate voxels into surface and bulk
- Compare dspacing to initial value (prior to gas)

$$\varepsilon_G\,(x,y,z) = \frac{\varepsilon_i\,(x,y,z) - \varepsilon_0}{\varepsilon_0}$$

- Small variation in NP bulk
- Tensile surface strain increases over 20 s
- Returns to initial value within 2 minutes
- Observe oscillations
  - Thermal regulation **or**
  - Competitive adsorption?

Average strain change

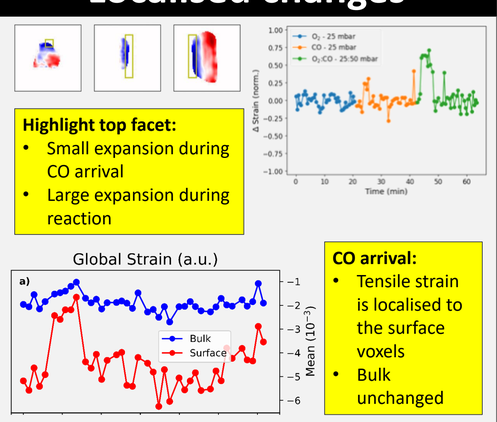


$$\gamma_1 = \frac{\sum w_i \cdot (x_i - \mu)^2}{\sigma^{3/2} \cdot \sum w_i}$$

Negative skew => more tensile strain

- Heterogenous strain
- Observe changes in strain variation and skewness during CO oxidation
- Skewness evolves over 2-3 scans (~1 min)

Localised changes



Highlight top facet:
- Small expansion during CO arrival
- Large expansion during reaction

CO arrival:
- Tensile strain is localised to the surface voxels
- Bulk unchanged

Conclusions:

We demonstrate how BCDI can be carried out in real time and with pump-probe techniques at a synchrotron [5]. The 3D strain profile shows the surface and sub-surface regions undergo the greatest change during the reaction with small changes in the bulk of nanoparticles. Depending on the initial conditions, the strain changes along the [111] direction can be further localised to specific facets, where we observe the rate of increase of tensile strain (τ = 7.0 s) at Pt {111} facets. With a benchmark figure of 0.25 s resolution, we observe oscillatory strain changes (T = 6.8 s) which may be related to site specific CO adsorption during the oxidation reaction.

[1] McEwen, J. S. *et al.* (2003) Surf. Sci. **545**, 47–69. [2] Marchesini, S. *et al.* (2003). Phys. Rev. B, **68**, 140101. [3] Dupraz, M. *et al.* (2022). Nat. Commun. **13**, 1–10. [4] Favre-Nicolin, V. *et al.* (2011). J. Appl. Cryst. **44**(3), 635–640 [5] Grimes, M. *et al.* (2023). In preparation.

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